HIS HIGHNESS THE MAHARAJA SIR SAYAJIRAO GAEKWAR III
Sena Khaskhel, Samsher Bahadur. G. C. S. I., G. C. I. E., LL. D ETC.

A Compilation of Research Contributions.

HUMBLE TRIBUTE

TO

HIS HIGHNE[redacted]THE MAHARAJA SIR SAYAJIRAO GAEKWAR III
Sena Khaskh[redacted] Samsher Bahadur. G. C. S. I., G. C. I. E., LL. D. ETC.

In Commemoration of the
DIAMOND JUBILEE CELEBRATIONS.

FROM

The Staff and the Students of the
Science Departments, Baroda College.

PHYSICS.

FOREWORD.

This volume consists of reprints of research papers published by members of the science departments of the College. They are collected from various scientific journals and represent original work done alone or in collaboration with students and other workers. Some of this work was done in laboratories in Europe but the greater portion of it was done in the Chemistry laboratories of the College under the guidance of Dr. K. G. Naik. Starting in a modest manner with limited facilities after his return with a D. Sc. degree from Europe in 1922, Dr. Naik has built up a strong school of research, and the output, both in quantity and quality, would be a credit to any institution. Many of his students as a result of the research work they did here, now occupy responsible positions in university colleges, technical institutes and factories.

The authors desired that these papers should be collected in one volume, for they feel that this record of their work may be regarded as a fitting tribute to His Highness the Maharaja Saheb whose constant encouragement of all educational effort has alone made such work possible.

Now that the opening of the Jubilee Science Institute gives far greater facilities for scientific work than the College has hitherto possessed it will be the aim of all our science men to make the utmost use of the opportunities offered, and to ensure that the delicate plant of research will flourish and become a vigorous tree.

Baroda, 30th Dec. 1935.

S. G. BURROW,
Principal, Baroda College.

H. E. Sir V. T. Krishnamachari,
Dewan Saheb. BARODA STATE.

INTRODUCTION.

The object in compiling the Research work done in the Science Departments was to present to our Ruler His Highness Sir Sayajirao Gaekwar III, Maharaja of Baroda, a small brochure containing the papers which are already published in the recognised Journals of Europe, America and India, as a humble tribute on the occasion of His Highness's Diamond Jubilee and the opening of the Sayaji Jubilee Institute. The papers embodied comprise the research work of the members of the staff either by themselves or in collaboration with their co-workers or students.

When the undersigned joined the Baroda State service in 1918, the Science Departments had scarcely enough accomodations and fittings for adequate full grade teaching. But under the sympathetic and fostering care of His Highness's Government, more accomodation and better fittings were soon coming forth. The struggles to do research work really began in 1922, after the return of the undersigned from Europe. Since then quite a number of students took their M. Sc. degree by Research. Of these, one got the Moos Medal and two got the R. R. Gold Medal, for the best research work in chemistry in their respective years. Nine out of the nineteen chemistry students who got their M. Sc., went to Europe at their own expense, and got their Doctorates, Ph. D. or D. Sc. degrees of London, Paris, Leeds, Berlin, and have done work which has been well spoken of by the leading chemists in Europe and America. Four of these young men are in the Baroda State service and are actively engaged in research. The other five are in the staff of other Colleges and the University of Bombay. The research work done by the staff of the Physics Department deals with problems in difficult subjects like, spectroscopy, ultra-short waves and atomic physics, for which degrees of M. Sc. and Ph. D. (London) have been conferred. Unfortunately the Head of the Department of Biology is ill and is in hospital. The

undersigned regrets that in his absence it was not possible to get the research work done in the Department by his colleagues and students, incorporated in the volume-researches for which the degrees of M.Sc. and D.Sc. (France) have been conferred.

His Highness the Maharaja Saheb and the Government, appreciating the efforts so far made by the Science Departments to make the best of the available resources decided to give increased facilities in all directions to carry forward their work. The fostering care of His Highness and the abiding sympathy and keenness of H. E. the Dewan Saheb, Sir V. T. Krishnamachari, Kt., were mainly instrumental in bringing into existence the Sayaji Jubilee Institute. Several well-to-do and leading citizens offered, to H. E. the Dewan Saheb, large donations as contributions towards the memory of our Beloved Petron and Ruler, with the result that a technological wing for Industrial Research is also attached to the Institute. The undersigned and all his colleagues look forward with mingled feelings of anxiety and pride to fulfil adequately the extended trust so placed in them. Their only prayer is that the kindness and sympathy which they have so far enjoyed, may be ever continued in future. It is these that will strengthen them in their future increased efforts.

K. G. NAIK.

NAME OF STUDENTS.

1. **Mahadev Dattatraya Avasare,**
   M. Sc. (Bombay, 1923). Ph. D. (London, 1929),
   Professor of Chemistry, Baroda College.

2. **Chaturbhai Shankerbhai Patel,**
   M. Sc. (Bombay, 1925), Ph. D. (London, 1930),
   Lecturer in Chemical Technology,
   Kala-Bhavan, Baroda.

3. **Ganpatram Vishram Jadhav,**
   M. Sc. Distinction (Bombay, 1926),
   Lecturer in Chemistry, Royal Institute of
   Science, Bombay,
   (For Higher studies in England).

4. **Mohanlal Laxmidas Shah,**
   M. Sc. Distinction (Bombay, 1926),
   Demonstrator in Chemistry, Baroda College.

5. **Yeshwant Narayan Bhat,**
   M. Sc. Distinction (Bombay, 1926),
   Asst. Head Master and Science Teacher,
   High School, Kolhapur.

6. **Chimanlal Himatlal Shah,**
   M. Sc. Distinction (Bombay, 1928),
   Chemist, Alembic Chemical Works, Baroda.

7. **Ramniklal Keshavlal Trivedi,**
   M. Sc. Distinction (Bombay, 1928) R. R. Desai
   Gold Medalist, D. és Sc., Mention Très Honorable.
   (France, 1932),
   Lecturer in Chemistry, Baroda College.

8. **Haribhai Ranchhodji Desai,**
   M. Sc. (Bombay, 1928),
   Asst. Conservator of Forest, Baroda State.

9. **Mukundrai Maneklal Parikh,**
M. Sc. Distinction (Bombay, 1929),
Ph. D. (London, 1932); F. I. C.,
Professor of Chemistry, Samaldas College,
Bhavnagar.

10. **Chandulal Chhotalal Shah,**
M. Sc., Distinction, (Bombay, 1929), R. R. Desai
Gold Medalist, Ph. D. (London, 1932).
Lecturer in Chemistry, Baroda College.

11. **Lallubhai Dahyabhai Shah,**
M. Sc., Distinction (Bombay, 1930),
Ph. D. (London, 1933).
Professor of Chemistry, M. T. B. Arts College
Surat.

12. **Padmakant Narsingrao Desai,**
M. Sc. Distinction (Bombay, 1930) Deceased, 1931.

13. **Vishnu Bapurao Thosar,**
M. Sc., Distinction (Bombay, 1931).
University Department of Chemical Technology
Bombay.

14. **Ratilal Prabhudas Patel,**
M. Sc., Distiuction (Bombay, 1931) Moos Medalist.
Chemist, Alembic Chemical Works, Baroda.
(at present in England for higher studies in
Pharmacological Chemistry).

15. **Kanaiyalal Darottamdas Chokshi,**
M. Sc., Distinction (Bombay, 1932).

16. **Bansidhar Vithaldas Mehta,**
M. Sc., (Bombay, 1932).
Lecturer in Chemistry, Kala-Bhavan, Baroda.

17. **Shantirai Anantrai Vaishnav,**
M. Sc., (Bombay, 1933).
Science Teacher, High School, Junagadh.

18. **Sakarlal Mathurdas Gaywala,**
M. Sc., (Bombay, 1934).
Science Teacher, High School, Sinor.

19. **Ambalal Dahyabhai Patel,**
M. Sc., (Bombay 193[illegible])
Cotton & Yarn Merchant, Madura.

20. **Chhaganlal Motiram Mehta,**
M. Sc., (Bombay, 1935)
Lecturer in Chemistry, Baroda College.

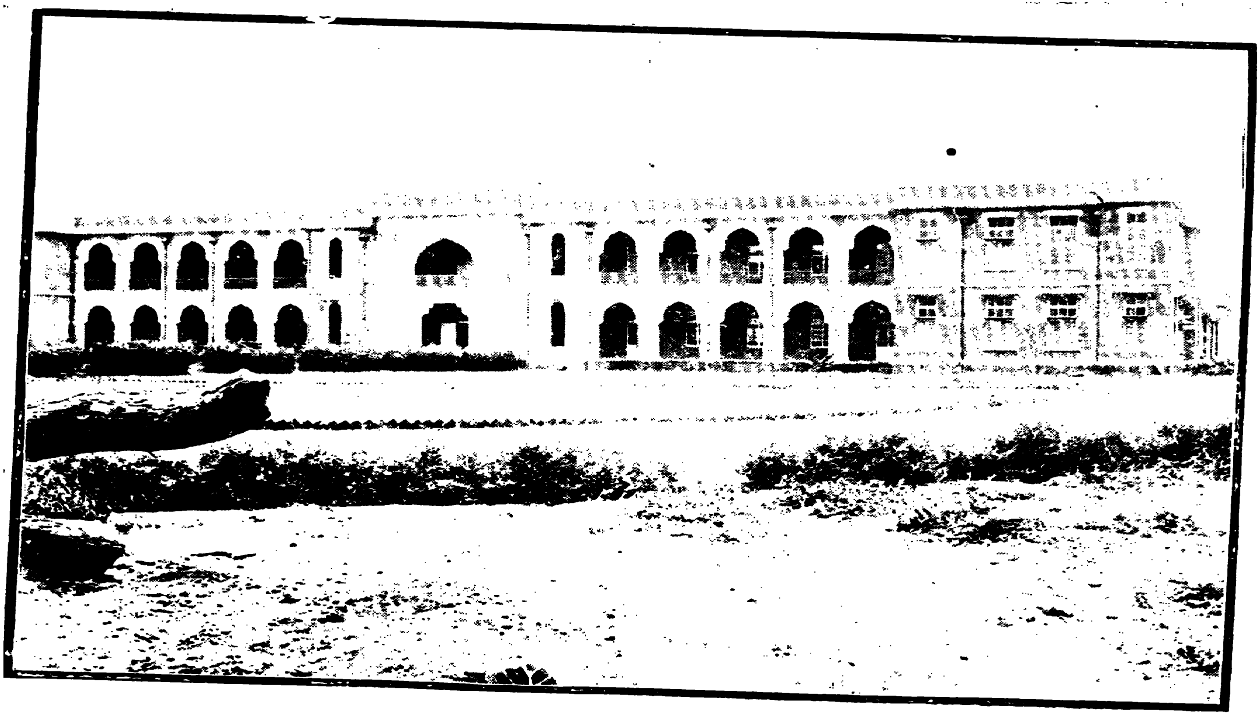
21. **Sakarlal Vrajlal Shah,**
Ph. D. (Göttingen, 1927).
Professor of Chemistry, Rajaram College,
Kolhapur.

22. **Thakorbhai Naranji Mehta,**
Ph. D. (London, 1931).
University Department of Chemical Technology,
Bombay.

23. **Mahendra Harilal Desai,**
Ph. D. (London, 1932).
Asstt. Chemist, Behar Sugar Works, Pachrukhi.

24. **Yeshwantrai Gulabbhai Naik,**
M. Sc., (Bombay, 1933).
Lecturer in Physic R. I. S., Bombay.

25. **Shreedhar Raghunath Lele,**
M. Sc., (Bombay 1934),
Bombay.



SHREE SAYAJI JUBILEE INSTITUTE.

I. *The Formation and Properties of Dithioketones* ($R_2C:S:S$) *and Dithio-ethers* ($R_2S:S$). *Part I*

By KUVERJI GOSAI NAIK.

The formation of "mustard gas" ($\beta\beta'$-dichlorodiethyl sulphide) by the sulphur chloride process may be represented by the scheme ;

$$2CH_2{:}CH_2 + Cl_2S{:}S \begin{cases} \nearrow (CH_2Cl{\cdot}CH_2)_2S{:}S \quad \text{(I.)} \\ \searrow (CH_2Cl{\cdot}CH_2)_2S + S. \quad \text{(II)} \end{cases}$$

Certain difficulties were initially encountered owing to the condition in which the second sulphur atom occurred in the product. If the reaction between sulphur monochloride and ethylene is carried out under the right conditions the second atom of sulphur is deposited in the elemental form, but under other conditions it remains either in solution in or in combination with the sulphide (II). The question whether the compound (I) is stable under ordinary atmospheric conditions is a vital one, because the vapour tension of "mustard gas" is already so low as to place it on the line limiting the usefulness in war of toxic substances which rely for their effect on the amount of vapour introduced into the air under normal conditions of temperature and pressure. If the second sulphur atom remained in chemical combination, as in formula I, the vapour tension of the compound would be lower than that of "mustard gas," and its utility as a toxic agent would thereby be diminished, if not entirely destroyed.

The late Lieut.-Col. Harrison showed that the product containing the two sulphur atoms vaporised completely at the ordinary temperature, leaving only a residue of sulphur, and that the vapour evolved at different periods of the evaporation had the same order of toxicity as "mustard gas."

There is thus no doubt that the second sulphur atom in the product of the action of sulphur monochloride on ethylene behaves as if it were in solution in, and not in chemical combination with, the sulphide, and the objects of the present series of investigations are to show to what degree the instability of the dithio-grouping is affected by the molecular condition of the remainder of the molecule and to compare the relative stability exhibited by corresponding dithio-ketones of the general formula $R_2C:S:S$.

The first compound of the dithio-ketone series (III) was prepared by the action of sulphur monochloride on malonanilide in accordance with the equation :

$$(NHPh{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(III.)}}{(NHPh{\cdot}CO)_2C{:}S{:}S} + 2HCl.$$

The formula given to it above is proved by the following considerations :

(1) It is a dithio-ketone, that is, it is formed from one molecule of the anilide and one molecule of sulphur monochloride with the elimination of two hydrogen atoms as hydrogen chloride.

(2) The two hydrogen atoms are not supplied by the phenyl groups, because a dithio-ketone (IV) is produced from malondi-methylamide by a similar reaction :

$$(NHMe{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(IV.)}}{(NHMe{\cdot}CO)_2C{:}S{:}S} + 2HCl$$

also

$$(CH_2Ph{\cdot}NH{\cdot}CO)_2CH_2 + Cl_2S{:}S = \underset{\text{(V.)}}{(CH_2Ph{\cdot}NH{\cdot}CO)_2C{:}S{:}S} + 2HCl$$

(3) The two hydrogen atoms eliminated are not those which were originally attached to the two nitrogen atoms, because when sulphur monochloride reacts with methylmalonanilide (VI)—which, it will be noted, cannot form a dithio-ketone on the methine carbon atom, but can readily do so if the two hydrogen atoms attached to nitrogen are those affected—there is formed a disulphide (VII) in accordance with the equation:

$$2CHMe(Co{\cdot}NHPh)_2 \xrightarrow{Cl_2S:S} S{:}S{<}\begin{matrix}CMe(CO{\cdot}NHPh)_2\\CMe(CO{\cdot}NHPh)_2\end{matrix}.$$

(VI.) (VII.)

Similar disulphides are produced when tertiary alkylated amides are employed. Thus the disulphide (VIII) is produced from malondimethylanilide:

$$2CH_2(CO{\cdot}NMePh)_2 \longrightarrow S{:}S{<}\begin{matrix}CH(CO{\cdot}NMePh)_2\\CH(CO{\cdot}NMePh)_2\end{matrix}.$$

(VIII.)

It should be added that these disulphides, unlike the dithio-derivative of " mustard gas " to which they are apparently related in composition, are stable substances. They are at present under investigation.

(4) The dithio-ketones behave on hydrolysis in a manner which is in accordance with that which might be expected from the proposed formula. Thus, dithiomesoxanilide (III), on hydrolysis with alkali hydroxide yields aniline and the alkali salt of a dithioacid which probably has the structure IX, because it yields hydrogen sulphide by treatment with mineral acids:

$$S{:}S{:}C(CO{\cdot}NHPh)_2 \xrightarrow{KOH} PhNH_2 + S{:}S{:}C(CO_2K)_2.$$

(III.) (IX).

(5) When dithiomesoxanilide (III) is treated with bromine, sulphur bromide is produced, together with the compound (X), which is identical with that formed by the action of bromine on malonanilide (Backes, West, and Whiteley, J. C. S., 1921, **119**, 373). It is evident therefore that the reaction takes place thus:

$$S{:}S{:}C(CO{\cdot}NHPh)_2 + 3Br_2 \rightarrow SBr{\cdot}SBr{:}C(CO{\cdot}NH{\cdot}C_6H_4Br)_2 + 2HBr.$$
$$\rightarrow S_2Br_2 + CHBr(CO{\cdot}NH{\cdot}C_6H_4Br)_2.$$

(X.)

(6) On reduction with an alkaline solution of sodium hydrosulphide dithiomesoxanilide is transformed into malonanilide and hydrogen sulphide:

$$S{:}S{:}C(CO{\cdot}NHPh)_2 + 6H = 2H_2S + CH_2(CO{\cdot}NHPh)_2.$$

(7) The action of sulphur monochloride on diphenylbarbituric acid also yields a dithio-ketone (XI):

$$CH_2{<}{\begin{matrix}CO{\cdot}NPh\\CO{\cdot}NPh\end{matrix}}{>}CO \xrightarrow{Cl_2S:S} S{:}SC{<}{\begin{matrix}CO{\cdot}NPh\\CO{\cdot}NPh\end{matrix}}{>}CO.$$

(XI.)

It is clear, therefore, that the formulæ assigned to the dithio-ketones are correct. It may be added that their stability is such that the action of fuming nitric acid on, for example, dithiomesoxanilide leads to the formation of a tetranitro-compound (XII) and leaves the dithio-group intact:

$$S{:}S{:}C(CO{\cdot}NHPh)_2 \longrightarrow S{:}S{:}C(CO{\cdot}NH{\cdot}C_6H_3[NO_2]_2)_2$$

(XII.)

Already, therefore, compounds of both dithio-ketone and dithio-ether types have been isolated which exhibit a degree of stability altogether different from that of the hypothetical dithio-derivative formed in the "mustard gas" reaction. It is perhaps too soon to draw any definite conclusion, but the difference is so great that one is forced to consider whether in these reactions sulphur monochloride may not react in two forms, namely, SCl·SCl and $Cl_2S{:}S$. This question has led to much controversy, and the general opinion at the present time is that the second formula is the correct one. Indeed, it would be difficult to explain the formation of "mustard gas" on any other assumption. Still, if it can be assumed that the reagent can react in either form according to the conditions of the experiment and that in the experiments described in the present paper it reacts in the form of SCl·SCl, the dithio-ketones and the disulphides would have the formulæ $\begin{matrix}S\\|\\S\end{matrix}{>}C(CO{\cdot}NHPh)_2$ and $\begin{matrix}S{\cdot}CH(CO{\cdot}NHPh)_2\\|\\S{\cdot}CH(CO{\cdot}NHPh)_2\end{matrix}$ respectively, and compounds of the latter type, for example, dithiosalicylic acid (Friedländer), are known to have a high order of stability. These questions will form the subject of further investigation.

Experimental.

Dithiomesoxanilide (III).

Nine grams of malonanilide and 10 grams of sulphur monochloride (S_2Cl_2) were heated under reflux with 50 c. c. of dry benzene. As soon as the benzene began to boil, hydrogen chloride gas was vigorously evolved. After three hours the evolution ceased and the product was filtered and washed thoroughly with dry benzene to free it from the excess of sulphur monochloride. The solid residue, which was almost pure and appeared to be free from any precipitated sulphur. was difficultly soluble in acetone, from which it crystallised in short, colourless needles, m. p. 214—215° (Found: N = 8.70; S = 20.10. $C_{15}H_{12}O_2N_2S_2$ requires N = 8.86; S = 20.25 per cent).

Two grams of this substance were boiled under reflux with a large quantity of absolute alcohol for two hours in order to determine whether either of the sulphur atoms was separable. The solid, after filtration, was repeatedly extracted with carbon disulphide (Found : N = 9.12; S = 20.33 per cent.)

In order to see if the reaction took place in two stages, only half the quantity of sulphur chloride theoretically required was added to malonanilide and the condensation allowed to take place under the same conditions as before. The product was repeatedly boiled with alcohol to free it from any unchanged malonanilide. Almost one-half of the malonanilide was recovered and the other half was completely converted into a dithio-ketone. Thus the reaction appears to take place in one stage only, the substance $[CH(CO{\cdot}NHPh)_2]_2S_2$ not being formed.

Nitration of Dithiomesoxanilide.—A very vigorous reaction occurred when 5 grams of the anilide were treated with nitric acid (D 1.5), and the whole of the substance dissolved, The nitrated product slowly separated in fine crystals on further warming. It was collected, washed with concentrated

nitric acid and with water, and dried, and then melted at 232—233° (Found : N = 16·72; S = 12·60. $C_{18}H_{8}O_{10}N_{6}S_{2}$ requires N = 16·93; S = 12·90 per cent.).

Hydrolysis of Dithiomesoxanilide.—The anilide (15 grams) was hydrolysed by boiling for two hours under reflux with a solution of potassium hydroxide (10 grams) in water (16 grams). The aniline produced by the hydrolysis was extracted with ether and identified. From the aqueous solution a solid was isolated which reacted with hydrochloric acid to produce hydrogen sulphide, and was evidently potassium sulphide which had been formed during the hydrolysis.

Bromination.—Ten grams of dithiomesoxanilide (1 mol.) were treated with bromine (rather more than 3 mols.) in glacial acetic acid solution. The product, after spontaneous evaporation of the acetic acid, smelt of sulphur bromide. When the smell became faint the product was boiled with alcohol under reflux. The solution deposited on cooling light, white tufts, which melted sharply at 239° after repeated crystallisation. The substance was found to be identical with the tribromomalonanilide prepared by the direct bromination of malonanilide (Backes, West, and Whiteley, J. C. S., 1921, **119**, 373).

Reduction of dithiomesoxanilide.—Malonanilide, m. p. 224—225°, was produced when dithiomesoxanilide (10 grams), dissolved in boiling alcohol (100 c.c.), was reduced by an alkaline solution of sodium sulphide by Brand's method (*Ber.*, 1909, **42**, 3464).

Dithiomesoxodimethylamide (IV).

This substance, prepared from malondimethylamide (1·5 grams) and sulphur monochloride (about 2 grams) in the same way as dithiomesoxanilide, was difficultly soluble in absolute alcohol. It separated from a concentrated solution

in slender needles and ultimately as a crystalline powder which melted at 216—217° (Found : N = 14·24; S = 33·24. $C_6H_8O_2N_2S_2$ requires N = 14·58; S = 33·33 per cent.).

Dithiomesoxodibenzylamide (V).

This substance was prepared from 4 grams of malondibenzylamide and 2 grams of sulphur hloride. The product was dissolved in absolute alcohol, from which it separated in fine, white crystals melting at 204° (Found : N 8·57; S = 18·18. $C_{17}H_{16}O_2N_2S_2$ requires N = 8·34; S = 18·61 p. c.).

Malondimethylanilide Disulphide (VIII).

A mixture of 5 grams of malondimethylanilide. 50 grams of dry benzene, and 2·7 grams of sulphur chloride was heated under reflux for three hours. The action was not so vigorous as in the case of malonanilide. The product was washed with dry benzene to remove the unchanged sulphur monochloride, dissolved in hot acetic acid, and precipitated from the solution by hot water. This treatment was repeated until the substance had a constant melting point, 218—219° (Found : S = 10·52. $C_{34}H_{34}O_4N_4S_2$ requires S = 10·22 p. c.).

Methylmalonanilide Disulphide (VII).

Methylmalonanilide was prepared by heating a mixture of methyl methylmalonate (17 grams) and aniline (19 grams) for five hours at 140° and finally at 150—160° until the distillation of methyl alcohol ceased. After crystallisation from alcohol the product melted at 180°.

A mixture of 10 grams of methylmalonanilide, 100 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux. Evolution of hydrogen chloride began to take place at once. After three hours, the solid was collected, washed with dry benzene, and crystallised from absolute alcohol, when it was obtained as a crystalline powder melting at 229—230° (Found : S = 11·01. $C_{32}H_{30}O_4N_4S_2$ requires S = 10·70 per cent.).

5-Disulphido-1 : 3-diphenylbarbituric acid (XI).

Sulphur monochloride (2·7 grams) dissolved in a small quantity of benzene was gradually added to a boiling mixture of benzene (50 c. c.) and diphenylbarbituric acid (5·6 grams). The acid, which was not soluble in benzene, rapidly disappeared and hydrogen chloride was evolved. After two hours, the brown liquid was cooled and filtered, and the solvent allowed to evaporate. The residue was again dissolved in benzene and, after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum, when it melted sharply at 181°. The molecular weight, determined by the cryoscopic method in benzene solution, was 355·5 (Found : S = 19·20. $C_{16}H_{10}O_3N_2S_2$ requires S = 18·72 per cent. ; M = 342).

In conclusion, I take this opportunity of expressing my sincere gratitude to Prof. J. F. Thorpe and Dr. M. A, Whiteley for the keen interest they have shown and the kind encouragement they have given me throughout this work. I also express my thanks to the Chemical Society for a grant from their Research Fund, which has partly defrayed the expenses incurred in this investigation.

Imperial College of Science and Technology;
South Kensington.

(Reprinted from the Transactions of the Chemical Society, 1921, Vol, 119).

II. Interaction of Sulphur Monochloride and Organic Acid Amides.

By Kuverji Gosai Naik.

The reaction of acid chlorides with amides, amines, and their derivatives appears to have been extensively studied. In particular, a number of investigations on the interaction of various amines and sulphur monochloride have been carried out (Claus and Krall, *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445; Schmidt, *Ber.*, 1878, **11**, 1168; Michaelis, *Ber.*, 1895, **28**, 165), but no systematic study of the interaction of sulphur monochloride and organic acid amides or their substituted derivatives appears to have been made.

The reaction of sulphur monochloride with dry ammonia gas is very vigorous. When sulphur monochloride is dropped into the gas, flashes of light are produced and heavy clouds of ammonium chloride are developed, with the simultaneous deposition of sulphur.

In view of this it is to be expected that—

(i) The amido-group in the organic amides will readily react with sulphur monochloride and give rise to sulphides:

$$\begin{matrix}-NH_2\\-NH_2\end{matrix}+\begin{matrix}Cl\\Cl\end{matrix}>S{:}S \longrightarrow \begin{matrix}-NH\\-NH\end{matrix}>S{:}S \longrightarrow \begin{matrix}-NH\\-NH\end{matrix}>S+S.$$

(ii) Amines will be more reactive than amides on account of their more strongly basic character.

(iii) Amides of the monocarboxylic acids, such as acetamide, may be expected to condense with sulphur monochloride more readily than the amides of the dicarboxylic acids, such as oxamide, because the two carbamyl groups in adjacent positions in the latter may be expected to increase

the acidity, and thus render the $-NH_2$ group in such amides less reactive.

These expectations have been fulfilled by the results of the present work. Oxamide, succinamide, malonamide, phthalamide, and phthalimide do not react with sulphur monochloride. Oxanilide also proved unreactive, whilst malonanilide condensed in the manner characteristic of $\cdot CO\cdot CH_2\cdot CO\cdot$ derivatives (J. C. S. 1921, **119**. 379.)

As regards the other amides which have been investigated, namely, acetamide, butyramide, benzamide, benzanilide, carbamtde, thiocarbamide, thiocarbanilide, and salicylamide, tt may be noted in the first place that carbamide gave chtefly ammonium chloride and sulphur, along with hydrogen chloride. The reactions with acetamide, butyrmide, and benzamide followed a very simple course, two molecules of the amide condensing with one molecule of sulphur monochloride to give a diamido-sulphide. Thus:

$$2CH_3\cdot CO\cdot NH_2 + Cl_2S{:}S = (CH_3\cdot CO\cdot NH)_2S + 2HCl + S.$$

The reaction with thiocarbanilide resulted in the condensation of two molecules of the anilide:

$$2CS{<}{}^{NHPh}_{NHPh} + 2Cl_2S{:}S = \underset{\text{(II.)}}{CS{<}{}^{NPh\cdot NPh}_{NPh\cdot NPh}{>}CS} + 4HCl + 4S.$$

This reaction is similar in many respects to that observed by Hector (*J. pr. Chem.*, 1892, (ii), **44**, 492; compare also Dodt, *Ber.*, 1906, **39**, 1014), who found that two molecules of an unsymmetrical disubstituted thiocarbamide condense under the influence of sulphur monochloride, giving a product from which the four hydrogen atoms have been eliminated,

$$NPhMe\cdot C{\lessdot}{}^{S-S}_{N\cdot N}{\gtrdot}C\cdot NPhMe \text{ or } NPhMe\cdot CS\cdot N{:}N\cdot CS\cdot NPhMe.$$

The reaction with thiocarbamide is specially interesting, as it can be explained on Werner's view of the constitution

of thiocarbamide. Werner (T., 1919, **115**, 1168) suggested that in a neutral solution thiocarbamide is present in two forms in equilibrium, thus:

$$(a)\ HN{:}C{<}^{NH_3}_{\underset{|}{}S} \quad \overset{\longrightarrow}{\longleftarrow} \quad HN{:}C{<}^{NH_2}_{SH}\ (b).$$

In the present case, the form (*b*) can be taken as the active modification, the reaction with sulphur monochloride being as follows:

$$2NH{:}C(NH_2){\cdot}SH + Cl_2S{:}S = \underset{(III.)}{[NH{:}C(NH_2){\cdot}S]_2S},2HCl + S.$$

Benzanilide reacts with sulphur monochloride to produce a trisulphide, $S(S{\cdot}C_6H_4{\cdot}NH{\cdot}COPh)_2$, similar to that resulting from acetanilide and sulphur monochloride (Schmidt, *loc. cit.*), whilst salicylamide produces a disulphide,

$$NH_2{\cdot}CO{\cdot}C_6H_3(OH){\cdot}S{\cdot}S{\cdot}C_6H_3(OH){\cdot}CO{\cdot}NH_2.$$

Although phthalimide has no action on sulphur monochloride, its potassium derivative reacts to form a di-iminosulphide,

$$2C_6H_4{<}^{CO}_{CO}{>}NK + Cl_2S{:}S = \left[C_6H_4{<}^{CO}_{CO}{>}N\right]_2S + 2KCl + S.$$

Experimental.

N-*Sulphidobisacetamide* (I).

Sulphur monochloride (25 grams), dissolved in a small quantity of benzene, was gradually added to a boiling solution of acetamide (10 grams) in dry benzene (200 c.c.). The reaction began at once with the slow evolution of hydrogen chloride. After six hours, the undissolved white mass was collected, washed with dry benzene to remove the undecomposed sulphur monochloride, and crystallised from alcohol, from which the product separated in slender needles, m. p. 192°.

The compound dissolved readily in hot water, and decomposed aqueous sliver nitrate with the formation of silver sulphide. A solution in sodium carbonate, on boiling and then acidifying, evolved hydrogen sulphide (Found : S=21.48; N=19.27. $C_4H_8O_2N_2S$ requires S=21.62; N=18.92 per cent.)

N-*Sulphidobisbenzylamide*, $(C_6H_5CONH)_2S$

This substance was prepared from benzamide (10 grams) and sulphur monochloride (11 grams) in the same way as the preceding sulphide. The white, amorphous solid was sparingly soluble in benzene, from which it crystallised in fibrous needles melting at 188°. The product was insoluble in water and reacted neither with sodium carbonate solution nor with silver nitrate (Found : S = 11.90; N = 10.14. $C_{14}H_{12}O_2N_2S$ requires S = 11.76; N = 10.29 per cent.).

N-*Sulphidobisbutyramide*, $(C_3H_7CONH)_2S$

This substance, prepared from butyramide (5 grams) and sulphur monochloride (5 grams), in presence of dry benzene (50 c.c.) in the same way as the sulphidobisacetamide, was deposited as a solid very sparingly soluble in benzene, from which it separated in minute white crystals melting sharply at 175° (Found : N = 13.41; S = 16.05. $C_8H_{16}O_2N_2S$ requires N = 13.72; S = 15.68 per cent.).

Sulphidodithiocarbamide Dihydrochloride (III).

Sulphur monochloride (7 grams) was slowly run into a boiling solution of thiocarbamide (9 grams) in absolute alcohol (100 grams) previously saturated with sulphur monochloride. When the vigorous reaction had abated, the mixture was boiled for three hours and the hard yellow mass collected and extracted with a large quantity of alcohol and carbon disulphide until no more sulphur was removed. The resulting, pale yellow substance was insoluble in chloroform, ethylene dichloride, benzene, light petroleum, acetic acid,

carbon tetrachloride, or nitrobenzene, and melted with decomposition at 176—177°. On keeping under water it slowly deposited sulphur, hydrochloric acid being simultaneously formed. On treatment with sodium carbonate carbon dioxide was evolved. Sodium hydroxide first precipitated sulphur, which then dissolved in excess of the boiling alkali, from which, on acidification, hydrogen sulphide was evolved. On treating the aqueous solution with silver nitrate, silver chloride was at once precipitated, but it immediately darkened on the addition of concentrated ammonia owing to the formation of silver sulphide (Found : S = 37·12; Cl = 28·30; N = 22·00. $C_2H_6N_4S_3,2HCl$ requires S = 37·63; Cl = 28·62; N = 21·96 per cent.).

3 : 6-*Dithio*-1 : 2 : 4 : 5-*tetraphenylhexahydro*-1 : 2 : 4 : 5-*tetrazine* (II.)

A mixture of thiocarbanilide (8 grams), sulphur monochloride (5 grams), and dry benzene (200 c.c.) was boiled for three hours, when the solid was collected and washed repeatedly with dry benzene to remove any excess of sulphur monochloride. The substance was then dissolved in benzene, the solution treated with reduced copper until the free sulphur had been eliminated, and evaporated until prismatic crystals, melting sharply at 160°, were deposited. The mixture with thiocarbanilide melted at 138°.

The tetrazine is stable and is not affected by water, in which it is insoluble (Found : C=68·39; H=4·50; N=12·90; S=14·67. $C_{26}H_{20}N_4S_2$ requires C=69·02; H=4·42; N=12·39; S=14·15 per cent.).

Trisulphidobisbenzanilide, $S(S{\cdot}C_6H_4NH{\cdot}COPh)_2$.

Reaction quickly set in when benzanilide (14 grams) was heated with sulphur monochloride (10 grams). The dark brown solid formed was washed with dry petroleum and then precipitated from an alcoholic solution by means of

water. The yellowish-white precipitate was purified in benzene solution by reduced copper as in the last experiment. and was obtained as a flocculent precipitate, m. p. 244° (Found : N=5·98; S=20·17. $C_{26}H_{20}O_2N_2S_3$ requires N=5·74; S=19·67 per cent.)

Disulphidobis-salicylamide, $S_2[C_6H_3(OH)\cdot CO\cdot NH_2]_2$.

A mixture of 5 grams of salicylamide, 50 c.c. of dry benzene, and 5 grams of sulphur monochloride was heated under reflux for three hours. The product was washed with dry benzene and caused to separate several times from methyl alcohol by spontaneous evaporation. It was thus obtained as a yellow, amorphous solid which melted and decomposed at 226° (Found : S=18·51. $C_{14}H_{12}O_4N_2S_2$ requires S=19·04 per cent.).

N-Sulphidodiphthalimide, $\left[C_6H_4{<}^{CO}_{CO}{>}N\right]_2S$.

The dried potassium salt (compare Landsberg, *Annalen*, 1882, **215**, 181) of phthalimide (two mols.) and sulphur monochloride (one mol.) were heated with dry light petroleum under reflux for one hour. The residue was repeatedly extracted with dry light petroleum and finally purified by treatment with reduced copper in benzene as in the previous cases. The compound was thus obtained as white crystals which melted at 190°, and decomposed on keeping (Found : N=8·41; S=9·64. $C_{16}H_8O_4N_2S$ requires N=8·64; S=9·87 p. c.).

In conclusion, I have very great pleasure in recording my thanks to Prof. J. F. Thorpe and Dr. M. A. Whiteley for their keen interest and kind encouragement throughout the progress of this work, and to the Chemical Society for a grant from their Research Fund which has partly defrayed the expenses incurred in this investigation.

Imperial College of Science and Technology;
South Kensington.

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III. *The Formation and Properties of Dithioketones ($R_2C:S:S$) and Dithio-ethers ($R_2S:S$) Part II.*

By KUVERJI GOSAI NAIK.

THE experiments described in this paper afford clear evidence that the interaction of sulphur monochloride with compounds containing the methylene radicle depends on the nature of the groups attached to the two remaining valencies of the carbon atom. Thus, if these valencies carry neutral groups such as $CO{\cdot}NH_2$, for example, in malonamide, $CH_2(CO{\cdot}NH_2)_2$, no reaction occurs. If, however, one of these carboxyamido-groups is replaced by the carbethoxy-group, as in ethyl malonamate, $CH_2(CO_2Et){\cdot}CO{\cdot}NH_2$, or if the neutral character of either or both of the carboxyamido-groups is disturbed by the substitution of a phenyl, tolyl, or similar group at the nitrogen atom, as in the compounds $CH_2(CO{\cdot}NH_2){\cdot}CO{\cdot}NHPh$, $CH_2(CO{\cdot}NH{\cdot}C_{10}H_7)_2$, $CH_2(CO{\cdot}NH{\cdot}C_7H_7)_2$, interaction with sulphur monochloride readily occurs with the formation of dithioketones of the type $S:S:C(CO{\cdot}NH_2){\cdot}CO{\cdot}NHPh$.

Moreover, although no definite measurements have as yet been made, it is evident that the speed of the reaction depends on the electronegative character of the attached groups. For example, sulphur monochloride reacts more vigorously with malondiphenylamide, $CH_2(CO{\cdot}NHPh)_2$, than with malonomonotolylamide, $CH_2(CO{\cdot}NH_2){\cdot}CO{\cdot}NH{\cdot}C_7H_7$, and the reaction with ethyl malonotolylamate, $CH_2(CO_2Et)CO{\cdot}NH{\cdot}C_7H_7$, is still more vigorous than with either of the former compounds. In fact, reactions of the last-named type take place at the ordinary temperature with copious evolution of hydrogen chloride.

Wolff and Ott (*Ber.*, 1903, **36**, 3721) have studied the interaction of methyl and ethyl malonates with sulphur monochloride in the presence of anhydrous aluminium chloride and obtained different compounds with the two esters. Since it is well known that sulphur monochloride reacts in different ways under different conditions (Böeseken, *Rec. trav. chim.*, 1905, **24**, 209; Cohen and Skirrow, T., 1899, **75**, 887; P., 1899, **15**, 183; Claus and Krall *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445), it was decided to study its reaction with (1) malonic and cyanoacetic esters and (2) their sodium compounds. It is remarkable that the products of these condensations are, in the case of the malonic ester, ethyl ethylenetetracarboxylate, and in the case of the cyanoacetic ester, ethyl dicyanosuccinate, whilst for the sodium compounds they are ethyl ethanetetracarboxylate in the case of the malonic ester, and ethyl dicyanosuccinate in the case of the cyanoacetic ester. A separation of sulphur occurs in every case:

$$2(EtO_2C)_2CHNa+S_2Cl_2=(EtO_2C)_2CH{\cdot}CH(CO_2Et)_2+2NaCl+2S.$$

$$2(EtO_2C)_2CH_2+2S_2Cl_2=(EtO_2C)_2C{:}C(CO_2Et)_2+4HCl+4S$$

and

$$2\,{}^{CN}_{EO_2C}{>}CHX+S_2Cl_2={}^{CN}_{EtO_2C}{>}CH{\cdot}CH{<}{}^{CN}_{CO_2Et}+2XCl+2S$$

where X=H or Na.

It has been mentioned in Part I of this series (J. C. S. 1921, **119**, 382) that dithiomesoxanilide, when nitrated with fuming nitric acid, yields a tetranitro-derivative:

$$S{:}S{:}C(CO{\cdot}NHPh)_2 \rightarrow S{:}S{:}C(CO{\cdot}NH{\cdot}C_6H_3[NO_2]_2)_2.$$

The reaction has now been extended to other dithioketones, for example, to dithiomesoxo-α-naphthylamide, which in the first place gives a tetranitro-derivative:

$$S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_7)_2 \rightarrow S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_5[NO_2]_2)_2.$$

When, however, nitration is carried further, the dithio-grouping is broken down and a sulphoxide results, two more nitro-groups entering the naphthalene nuclei at the same time

$$S{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_5[NO_2]_2)_2 \rightarrow O{:}S{:}C(CO{\cdot}NH{\cdot}C_{10}H_4[NO_2]_3)_2.$$

(I.)

Dithiomesoxo-β-naphthylamide and *o*- and *p*-toluidides behave in the same way.

An example of the nitration of a disulphide is furnished by methylmalono-*p*-toluidide disulphide, which, on very careful nitration, yields a dodecanitro-compound :

$$\begin{array}{l} S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_7)_2 \\ | \\ S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_7)_2 \end{array} \longrightarrow \begin{array}{l} S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_4[NO_2]_3)_2 \\ | \\ S{\cdot}CMe(CO{\cdot}NH{\cdot}C_7H_4[NO_2]_3)_2. \end{array}$$

(II.)

Clearly, therefore, it is possible to nitrate these compounds without destroying the dithio-grouping, which behaves as a remarkably stable residue. This is obviously a powerful argument in support of the view previously suggested that the dithio-grouping in these compounds is structurally different from that present in ββ'-dichlorodiethyl disulphide and similar compounds and that sulphur monochloride is capable of reacting in two forms,

$$(1)\ \begin{array}{l} S{\cdot}Cl \\ | \\ S{\cdot}Cl \end{array} \text{ and } (2)\ S{:}S{<}\begin{array}{l} Cl \\ Cl \end{array},$$

the first of which gives rise to very stable dithio-compounds (compare Part I of this series) containing the groups

$$\begin{array}{l} S \\ | \\ S \end{array}{>}C{<} \text{ and } \begin{array}{l} S{\cdot}C{\cdot} \\ | \\ S{\cdot}C{\cdot} \end{array}.$$

Experiments have been carried out with the object of testing the reactivity of sulphur monochloride towards compounds containing the group $-CO{\cdot}CH_2{\cdot}CO-$, when the latter forms a part of a closed ring, and as a large amount of work is being done in this laboratory on the formation and stability of spiro-compounds, it was decided to employ typical

spiro-compounds containing a cyclohexane ring. Three such compounds (III), (IV), and (V) (compare Norris and Thorpe, J. C. S., 1921, **119**, 1190) were selectsd :

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CH_2 \qquad Me_2C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CH_2$$

(III.) (IV.)

$$H_2C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>CH_2.$$

V.

The course pursued in these reactions affords a remarkable example of the difference in the behaviour of similarly constituted substances containing the $-CO\cdot CH_2\cdot CO-$ group towards sulphur monochloride. For, whilst in the compound (III) only one methylene group, namely, that situated between the carbonyl groups, is attacked, with the formation of the dithioketone (VI), in the compound (IV) the reaction proceeds further and involves one of the remaining methylene groups of the dihydroresorcinol ring, the substance (VII) being formed, and in the case of the *spiro*-compound (V), it proceeds yet further, all three of the methylene groups being attacked. The product in this case is the compound (VIII).

$$\begin{matrix}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CO\end{matrix}>C{:}S{:}S \qquad (VI.)$$

$$Me_2C<\begin{matrix}CH_2\cdot CO\\ CH—CO\end{matrix}>CS_2\ S_2C<\begin{matrix}CO\cdot CH_2\\ CO\cdot CH-\end{matrix}>CMe_2 \qquad (VII.)$$

$$|\underline{\qquad\qquad S-S \qquad\qquad}|$$

$$\overline{|\qquad\qquad S-S \qquad\qquad|}$$

$$H_2C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH\cdot CO\\ CH\cdot CO\end{matrix}>CS_2\ S_2C<\begin{matrix}CO\cdot CH\\ CO\cdot CH\end{matrix}>C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>CH_2$$

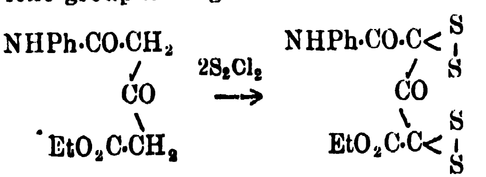
$$|\underline{\qquad\qquad S-S \qquad\qquad}|$$

(VIII.)

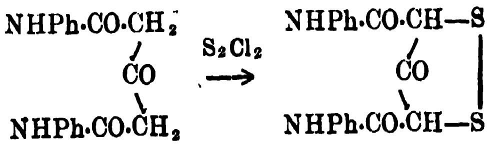
In order to obtain further knowledge of the influence on the reaction of sulphur monochloride with methylene groups of neighbouring electronegative residues, experi-

ments with substituted amides containing the group $-CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO-$ were made. The compounds employed were (1) the dianilide, (2) the di-*o*-toluidide, (3) the di-*p*-toluidide, of acetonedicarboxylic acid, and (4) ethyl-γ-phenylcarbamylacetoacetate.

Of these compounds, only (1) and (4) have been described (Besthorn and Garben, *Ber.*, 1900, **33**, 3443), whereas (2) and (3) do not appear to have been prepared. When these four compounds were treated with sulphur monochloride in dry benzene, reaction took place readily, but it was most vigorous in the case of compound (4), the product containing four atoms of sulphur. In cases (1), (2), and (3), although more than two molecules of sulphur monochloride were taken for every molecule of the substituted amide to give ample opportunity for the substitution of dithio-groups for all the hydrogen atoms in the two reactive methylene groups, reaction did not proceed to this extent and the product contained only two atoms of sulphur, one hydrogen atom of each methylene group having been substituted.



(IX)



(X.)

This is in accord with what follows from the hypothesis herein suggested, that the reactivity of the two hydrogen atoms of the methylene group is dependent on the total negativity of the two carbonyl groups with their attached radicles. It will be seen in the case of the foregoing substituted amides that the negative effect of the central carbonyl group is divided between the two adjacent methylene groups, so that the total negative effect on each methy-

lene group is smaller than that on a single methylene group when linked as $-CO \cdot CH_2 \cdot CO-$, as in the case of the compounds described in Part I. Hence it is to be expected that the two methylene groups in compounds (1), (2), and (3) will be less reactive than the methylene group in compounds such as malonanilide. However, as soon as the total negativity of the compound is increased by replacing one of the CO·NHR groups by a carbethoxy-group, the reactivity is correspondingly increased, and a dithio-compound is produced, analogous to those described above.

The investigation of the exact conditions under which the stability of the dithio-group can be controlled will be the subject of future work.

EXPERIMENTAL.

Dithiomesoxo-p-*toluidide*

Malono-p-toluidide was prepared by the method of Whiteley (T., 1903, **83**, 24) with the modification introduced by Roissert and More (Ber., 1906, **39**, 3300). The best temperature for the condensation is, in this instance, 140°, rising to 160°. The amide (10 grams), sulphur monochloride (5 grams) and benzene (100 grams) were heated together for three hours, and the solid condensation product was then washed with dry benzene and purified by precipitation from its solution in acetone by means of water until it melted at 215—216° (Found : S=18·26. $C_{17}H_{16}O_2N_2S_2$ requires S=18·60 per cent.).

The *tetranitro*-derivative was prepared by dissolving the thiocompound in sufficient nitric acid (D 1·5) and warming. The nitration product which separated on cooling was collected, washed with concentrated nitric acid and with water, and dried, when it was obtained as white crystals which melted and decomposed at 255° and assumed a yellow colour on keeping (Found : N=15·81; S=11·82. $C_{17}H_{12}O_{10}N_6S_2$ requires N=16·03; S=12·21 per cent.).

Dithiomesoxo-o-toluidide.

Malono-o-toluidide was prepared and condensed with sulphur monochloride similarly to the *para*-compound. The product obtained by evaporating the solvent (benzene) was crystallised from a mixture of benzene and light petroleum. It separated in fibrous needles melting at 189—190° (Found : S=18·89. $C_{17}H_{16}O_2N_2S_2$ requires S=18·60 per cent.).

The *tetranitro*-derivative was prepared in the same way as the p-isomeride and obtained as a yellowish-white powder when the solution in nitric acid was allowed to cool slowly. It melted and decomposed at 165° (Found : N=16·15; S=12·32. $C_{17}H_{12}O_{10}N_6S_2$ requires N=16·03; S=12·21 per cent.).

Dithiomesoxo-α-naphthylamide.

Malonodi-α-naphthylamide (6·5 grams), prepared like the toluidide except that the final temperature was 170°, sulphur monochloride (2·5 grams) and benzene (50 c.c.) were heated together and the product was purified by crystallisation from benzene. It formed pale red needles which sintered at 160° and melted with decomposition at 210° (Found : S=15·70, $C_{23}H_{16}O_2N_2S_2$ requires S=15·38 per cent.).

Tetranitro-derivative.—The dithio-amide (5 grams) was treated gradually with 40 c.c. of nitric acid (D 1·5). After the first violence of the reaction had abated, the mixture was warmed to complete it and then allowed to cool, when the tetranitro-compound separated as an orange-red powder. After being washed with concentrated nitric acid and with water, it melted at 190° with decomposition (Found: N=14·43; S=10·40. $C_{23}H_{12}O_{10}N_6S_2$ requires N=14·90; S=10·75 p. c.).

Hexanitro-sulphoxide (Formula 1).—This was recovered from the nitric acid washings by dilution with water as a yellow, crystalline substance which decomposed at 135° (Found : N=16·81; S=4·57. $C_{23}H_{10}O_{18}N_8S$ requires N=16·71; S=4·77 per cent.).

Dithiomesoxo-β-naphthylamide.

Malonodi-β-naphthylamide was prepared similarly to the ∝-compound and condensed in the same way. The product was purified by repeated precipitation by water from its solution in acetone until it melted at 204° with decomposition (Found: S = 15.56. $C_{23}H_{16}O_2N_2S_2$ requires S = 15.38 per cent.).

The *tetranitro*-derivative, when prepared and purified as in the case of the ∝-naphthylamide derivative, was obtained as a pale yellow powder decomposing at 195° (Found: N = 14.04; S = 10.54. $C_{23}H_{12}O_{10}N_6S_2$ requires N = 14.10; S = 10.73 per cent.).

*Dithiomesoxomono-*p*-toluidide.*

Malonomono-p-toluidide, prepared by Whiteley's method (loc. cit. Compare also Backes, West, and Whiteley, J. C. S. 1921, **119**, 372), the temperature of the condensation with p-toluidine being 120—125°, was condensed (7 grams) with sulphur monochloride (5 grams) in benzene (50 grams) in the usual manner. The product separated from alcohol, on addition of water, in short needles which melted to an oil clarifying at 150° and decomposing at 165° (Found: S = 24.78. $C_{10}H_{10}O_2N_2S_2$ requires S = 25.20 per cent.).

Dithiomesoxomonophenylamide.

Malonomonophenylamide, prepared like the toluidide, was condensed with sulphur monochloride in a similar way. The product separated from acetone, in which it was sparingly soluble, in short needles, melting and decomposing at 202° (Found: S = 26.9. $C_9H_8O_2N_2S_2$ requires S = 26.66 p. c.).

*Ethyl Dithiomesoxo-*p*-tolylamate*

Ethyl malono-p-tolylamate, prepared by Whiteley's method (ibid., pp. 36, 40) at 120—125°, was condensed (8 grams) with sulphur monochloride (5 grams) in benzene

(50 c. c.) in the usual way. The reaction began in the cold, with copious evolution of hydrogen chloride. The liquid was cooled and filtered and the solvent was allowed to evaporate. The semi-solid mass was redissolved in benzene, and solidified when the solution was cooled with ice. It sintered at 74° and melted at 90° (Found: S = 22.44. $C_{12}H_{13}O_3NS_2$ requires S = 22.61 per cent.).

Ethyl Dithiomesoxo-o-*tolylamate.*

This substance was prepared like the para-compound and was purified by repeated spontaneous evaporation of its solution in benzene and finally in ether. It melted at 62° (Fonnd: S = 22.48. $C_{12}H_{13}O_3NS_2$ requires S = 22.61 per cent).

Methylmalono-p-*toluidide Disulphide* Formula (II).

Methylmalono-p-*toluidide* was prepared from ethyl methylmalonate (9 grams) and *p*-toluidine (10 grams) in the same way as the lower homologue previously mentioned, except that in this case the temperature was 160° rising to 180°. It separated in a very pure condition and after crystallisation from acetic acid melted at 220° (Found: N = 9.79. $C_{18}H_{20}O_2N_2$ requires N = 9.46 per cent.).

The above amide (8 grams) and sulphur monochloride (2 grams) were allowed to react in benzene (100 c. c.) in the usual manner. The solution was cooled and filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and the product was crystallised from a mixture of benzene and light petroleum and then melted at 224—225° (Found: S = 10.19. $C_{36}H_{38}O_4N_4S_2$ requires S = 9.78 per cent.).

The *dodecanitro*-derivative was obtained by the regulated action of fuming nitric acid and precipitated by the addition of water. At no time should the liquid be allowed to boil. After being filtered and washed with nitric acid and with water, it was obtained as a pale yellow powder decomposing

at 140° (Found: N = 18·50; S = 5·61. $C_{36}H_{26}O_{28}N_{16}S_2$ requires N = 18·76; S = 5·36 per cent.).

Methylmalono-o-toluidide Disulphide.

Methylmalono-o-toluidide was prepared and purified like the *para*-compound. It melted at 161° (Found: N = 9·52 $C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.).

The amide was condensed with sulphur monochloride as in the case of the *para*-compound; the product crystallised from alcohol in mealy crystals which melted at 174° (Found: S = 10·09. $C_{36}H_{38}O_4N_4S_2$ requires S = 9·78 per cent.).

Methylmalonomono-o-toluidide Disulphide,

$S_2[CMe(CO{\cdot}NH_2){\cdot}CO{\cdot}NH{\cdot}C_7H_7]_2$.

Methylmalonomono-o-toluidide was prepared from ethyl methylmalonate (22 grams) and *o*-toluidine (9 grams) in a similar manner as malonomono-*p*-toluidide and was crystallised from dilute alcohol. It separated in pearly scales melting at 117° (Found : N=14·05. $C_{11}H_{14}O_2N_2$ requires N=13·60 per cent.).

This amide (6 grams) was condensed with sulphur monochloride (2 grams) in the presence of benzene (100 c.c.) as in the previous cases. The product was crystallised from a mixture of benzene and light petroleum, when it melted at 207—208° (Found : S=13·95. $C_{22}H_{26}O_4N_4S_2$ requires S=13·50 per cent.).

Methylmalonodimethylamide Disulphide, $S_2[CMe(CO{\cdot}NHMe)_2]_2$.

Methylmalonodimethylamide (Franchimont, *Rec. trav. chim.*, 1885, **4**, 204), when condensed (10 grams) with sulphur monochloride (5 grams) in benzene (100 c. c.), yielded a crystalline product which melted at 200° after being washed with benzene (Found: S = 18·72. $C_{12}H_{26}O_4N_4S_2$ requires S = 18·28 per cent.).

Interaction of Ethyl Sodiocyanoacetate and Sulphur Monochloride.

Ethyl sodiocyanoacetate, prepared from 25 grams of ethyl cyanoacetate, was refluxed for one hour with sulphur monochloride (15 grams) and dry benzene (100 c. c.). The dark solution on evaporation left an oil which, when distilled under reduced pressure, yielded a solid. After crystallisation from ether, this melted at 117—118°, contained no sulphur and was identified as ethyl dicyanosuccinate (Found: N = 12.76. Calc., N = 12.50 per cent.).

Interaction of Ethyl Sodiomalonate and Sulphur Monochloride.

Ethyl sodiomalonate, prepared from 50 grams of the ester, was refluxed with sulphur monochloride (0.5 mol.) in the manner described in the last experiment. The product, after crystallisation from ether, was identified as ethyl ethanetetracarboxylate (Found : C = 52.46; H = 6.57. Calc., C = 52.83; H = 6.91 per cent.).

Interaction of Ethyl Cyanoacetate and Sulphur Monochloride.

Ethyl cyanoacetate (20 grams) was heated on a water-bath with sulpur monochloride (25 grams) and the product obtained on cooling was extracted from the sulphur produced by a large quantity of ether. The solid obtained after evaporation of the solvent was crystallised from benzene. It melted at 117—118° and was identified as ethyl dicyanosuccinate.

Interaction of Ethyl Malonate and Sulphur Monochloride.

This condensation was conducted like the preceding, excepting that heating on a sand-bath was necessary to complete the reaction. The solid product was extracted with benzene and crystallised from light petroleum until it melted at 57—58°. It was identified as ethyl ethylenetetracarboxylate. The same product was obtained when benzene

was used as solvent and the product (an oil) subjected to distillation under reduced pressure.

Interaction of 1 : 1-*Dimethyl*cyclo*hexane*-3 : 5-*dione and Sulphur Monochloride* 3 : 5 : 3' : 5'-*Tetraketo*-4 : 4'-*bisdithio*-1 : 1 : 1' : 1'-*tetramethyldi*cyclo*hexyl* 2 : 2'-*Disulphide* (Formula VII).

The ketone (5 grams) and sulphur monochloride (10 grams) were allowed to react in boiling benzene (100 c. c.). The solution on cooling was filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum. when it softened at 110° and melted with decomposition at 150°. The molecular weight, determined by the cryoscopic method in benzene solution, was 472·5 (Found: S = 40·93. $C_{16}H_{18}O_4S_6$ requires S = 41·20 per cent.; M = 466).

Interaction of cyclo *Hexane*spirocyclo*hexane*-3 : 5-*dione and Sulphur Monochloride*. 1 : 1'-*Di*cyclo*hexane*spiro-3:5:3': 5'-*tetraketo*-4 : 4'-*bisdithiodi*cyclo*hexylene* 2 : 2' : 6 : 6'-*Bisdisulphide* (Formula VIII).

The ketone (2 grams), after being thoroughly dried in the steam oven for fifteen minutes, was heated under reflux with sulphur monochloride (3 grams) and dry benzene (100 c. c.). The product was isolated and purified in the same way as the preceding compound; it softened at 113° and melted and decomposed at 155°. The molecular weight, determined by the cryoscopic method in benzene solution, was 618 (Found: S = 41·72. $C_{22}H_{24}O_4S_8$ requires S = 42·10 per cent; M = 608).

Interaction of cyclo *Pentane*spirocyclo *hexane*-3 : 5-*dione and Sulphur Monochloride*. cyclo *Pentane* spiro-3 : 5-*diketo* 4-*dithio* cyclo *hexane* (Formula VI).

The ketone (2 grams) was boiled for two hours with sulphur monochloride (3 grams) dissolved in benzene (50 c. c.),

The product was isolated and purified as in the preceding cases; it softened at 114° and melted at 135°. The molecular weight, determined by the cryoscopic method in benzene solution, was 219 (Found : S=28·45. $C_{10}H_{12}O_2S_3$ requires S=28·07 per cent.; M=228).

αγ-Disulphidoacetonedicarboxydianilide (Formula X).

The acetonedicarboxydianilide required for the purpose was prepared by the method of Besthorn and Garbon (*loc cit.*) and purified by crystallisation from benzene. The more soluble ethyl γ-phenylcarbamylacetoacetate was recovered as a by-product from the residues.

A mixture of the dianilide (4 grams), sulphur monochloride (4 grams), and dry benzene (100 c. c.) was heated under reflux for two hours. The solution became deep red and hydrogen chloride was immediately evolved. The liquid was allowed to cool and the golden-yellow, crystalline product collected and recrystallised from benzene, when it melted at 220°. The molecular weight, determined by the cryoscopic method in benzene solution, was 343 (Found: N=8·15; S=18·41. $C_{17}H_{14}O_3N_2S_2$ requires N=7·82 S=17·87 per cent.; M=358).

Ethyl γ-Phenylcarbamyl-αγ-bisdisulphidoacetoacetate (Formula IX).

Ethyl γ-phenylcarbamylacetoacetate (4 grams) and sulphur monochloride (5 grams) were heated under reflux with dry benzene (50 c. c.). The red solution was filtered and the solvent allowed to evaporate, the residue being repeatedly dissolved in benzene and precipitated by light petroleum until it was pure. When heated, it sintered at 115° and melted with decomposition at 156—157°. The molecular weight, determined by the cryoscopic method in benzene, was 393·5 (Found : S=34·69. $C_{13}H_{11}O_4NS_4$ requires S=34·31 per cent,; M=373·0).

$\alpha\gamma$-*Disulphidoacetonedicarboxydi*-p-*toluidide.*

Preparation of Acetonedicarboxydi-p-*toluidide.*—Acetonedicarboxylic ester (25 grams) and *p*-toluidine (17·5 grams) were heated together in a sealed tube at 120° for twenty-four hours. When the contents of the tube were poured into benzene (500 c.c.) the *toluidide* separated in beautiful crystals, which, after recrystallisation from benzene, melted at 169—170° (Found : N=8·25. $C_{19}H_{20}O_3N_2$ requires N=8·64 per cent.).

A mixture of the amide (6 grams), sulpur monochloride (5 grams), and dry benzene (100 c.c.) was heated under reflux for two hours. The product, being sparingly soluble in benzene, separated from the hot solution in brilliant golden-yellow flakes which melted on recrystallisation at 216—217° (Found : S=16·14. $C_{19}H_{18}O_3N_2S_2$ requires S=16·58 p. c.),

$\alpha\gamma$-*Disulphidoacetonedicarboxydi*-o-*toluidide.*

Preparation of Acetonedicarboxydi-o-*toluidide.*—This substance was prepared in the same way as the corresponding *p*-tolyl derivative, and on recrystallisation from benzene melted at 167° (Found : N=8·86. $C_{19}H_{20}O_3N_2$ requires N=8·64 per cent.).

The amide was heated with sulphur monochloride in the same way as the corresponding *p*-compound. The product was sparingly soluble in benzene. from which it separated in brilliant orange crystals melting at 225° with decomposition (Found : S=16·88. $C_{19}H_{18}O_3N_2S_2$ requires S=16·58 p. c.).

In conclusion, I have very great pleasure in recording my thanks to Prof. J. F. Thorpe, Dr. M. A. Whiteley, and Mr. C. K. Ingold for their keen interest throughout this work, and to the Chemical Society for a grant which has partly defrayed the expense of this investigation.

The Imperial College of Science and Technology,
South Kensington.

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IV—The Formation and Properties of Dithioketones ($R_2C:S:S$) *and Dithio-ethers* ($R_2S:S$). *Part III.*

By KUVERJI GOSAI NAIK and MAHADEO DATTATRAYA AVASARE.

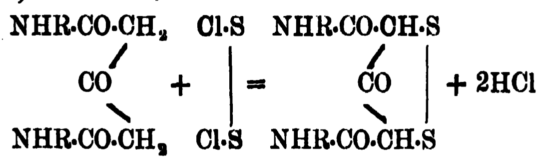
The experiments described here were undertaken with a view to test the hypothesis advanced by one of us (T., 1921, **119**, 1232), namely, that interaction of sulphur monochloride and a compound containing the methylene radicle depends on the nature of the groups attached to the two remaining valencies of the carbon atom. It was shown that either one or both of the hydrogen atoms of the methylene radicle were brought into activity, the course of the reaction depending on the total negativity of the two carbonyl groups with their attached radicles.

The work so far recorded was carried on with compounds which are derivatives of malonic or acetonedicarboxylic acid. Experiments have now now been made with (1) the anilide, (2) the *o*-toluidide and (3) the *p*-toluidide of acetoacetic acid. Of these compounds, only the first has been described (Knorr, *Annalen*, 1886, **236**, 75), whereas (2) and (3) do not seem to have been prepared. When these three compounds were treated with sulphur monochloride in dry benzene, reaction took place more readily and more vigorously than in the case of the corresponding derivatives of malonic and acetonedicarboxylic acids. Stable disulphides were formed in each case. Thus,

$$\begin{matrix}CH_3\cdot CO\\NHR\cdot CO\end{matrix}\!\!>CH_2+\begin{matrix}Cl\cdot S\\ |\\ Cl\cdot S\end{matrix}=\begin{matrix}CH_3\cdot CO\\NHR\cdot CO\end{matrix}\!\!>C<\begin{matrix}S\\ |\\ S\end{matrix}+2HCl,$$

where R is the phenyl or tolyl group. Here the total negativity of the groups attached to the reactive methylene group is greater than in the cases of the corresponding malonic and acetonedicarboxylic acid derivatives.

Considering the three compounds (i) $CH_3\cdot CO\cdot CH\cdot NHR$, (ii) $NHR\cdot CO\cdot CH_2\cdot CO\cdot NHR$, and (iii) $NHR\cdot CO\cdot CH_2\cdot CO\cdot CH_2\cdot CO\cdot NHR$, it will be seen that the total negativity of the carbonyl groups with their attached radicles in the case of (i) is due to two groups, one of which, $CO\cdot NHR$, is common to all three compounds, and the other, the acetyl group, is more negative than the partly neutralised group, $CO\cdot NHR$, which is present in (ii) and (iii). Again, the negative effect of the central carbonyl group in (iii) is divided between the two adjacent methylene groups, so that the total negative effect on each methylene group is smaller than that on a single methylene group, when linked as $-CO\cdot CH_2\cdot CO-$, as in cases (i) and (ii). Hence it is to be expected that the two methylene groups in (iii) will be less reactive than the one in (ii), which in turn will be less reactive than that in (i). Such has actually been found to be the case. Whereas compounds of type (iii) react thus,



those of types (ii) and (i) behave as follows,

$$\begin{matrix}NHR\cdot CO\\ R'\cdot CO\end{matrix}\!\!>CH_2+\begin{matrix}Cl\cdot S\\ |\\ Cl\cdot S\end{matrix}=\begin{matrix}NHR\cdot CO\\ R'\cdot CO\end{matrix}\!\!>C<\begin{matrix}S\\ |\\ S\end{matrix}+2HCl$$

where R' is the methyl or anilino-group. Reaction in the case of (i), however, proceeds very much faster than in the case of (ii), in fact, the reaction proceeds vigorously even in the cold. Such behaviour is in accordance with the thery.

It was stated in Parts I and II (*loc. cit.*, pp. 382, 1233) that it is possible to nitrate the compounds there mentioned without destroying the dithio-grouping, which behaves as a remakably stable residue. The dithio-compounds now described can also be nitrated in a similar way and give dinitro-derivatives :

$$C_6H_5\cdot NH\cdot CO\cdot CS_2\cdot CO\cdot CH_3 \longrightarrow C_6H_3(NO_2)_2\cdot CO\cdot CS_2\cdot CO\cdot CH_3$$

This behaviour obviously lends further support to the view

previously advanced that the dithio-grouping in these compounds is structurally different from that present in $\beta\beta'$-dichlorodiethyl disulphide and similar compounds, and that sulphur monochloride is capable of reacting in the two forms indicated (*loc. cit.*).

Further work is in progress with a view to throw additional light on the problem, by studying the influence of such reagents as sulphur dichloride, sulphuryl chloride, thionyl chloride, etc., on these and corresponding derivatives of cyanoacetic acid.

EXPERIMENTAL.

Dithioacetoacetanilide.—Two grams of acetoacetanilide and 2·5 grams of sulphur monochloride (S_2Cl_2) were heated under reflux with 50 c. c. of dry benzene for two hours. Reaction started in the cold, hydrogen chloride gas being vigorously evolved. When the evolution of the gas ceased, the product was filtered and washed thoroughly with dry benzene to free it from the excess of sulphur monochloride. The solid residue, after repeated purification from a mixture of benzene and petroleum, melted and decomposed at 125° (Found: S = 26·93. $C_{10}H_9O_2NS_2$ requires S = 26·78 per cent.).

The acetoacetanilide required for the experiment was prepared by Knorr's method (*loc. cit.*). The product obtained was very pure, but the yield was very small. It was crystallised from a mixture of benzene and ligroin.

The *dinitro*-derivative of the above dithioacetoacetanilide was prepared by warming the thio-compound with a sufficiency of nitric acid (*d* 1·5), reaction being very vigorous. The nitration product was precipitated by the addition of a minimum of water, and after being washed with nitric acid and with water was obtained as a brown powder, decomposing at 167° (Found: N = 12·90; S = 18·82. $C_{10}H_7O_6N_3S_2$ requires N = 12·76; S = 19·45 per cent.).

Acetoacet-p-*toluidide.*—Acetoacetic ester and *p*-toluidine in equimolecular quantities were heated in a sealed tube at

120—125° for five hours. The alcohol having been evaporated, the residue was cooled in a freezing mixture and the resulting crystalline mass washed with a mixture of benzene and ligroin and subsequently crystallised from the same solvent; the substance obtained melted at 95°. It is very soluble in alcohol or benzene and sparingly soluble in ligroin (Found: N = 7·56. $C_{11}H_{13}O_2N$ requires N = 7·33 per cent.).

Dithioacetoacet-p-*toluidide*.—Equal quantities (3 grams) of the above *p*-toluidide and sulphur monochloride were heated under reflux with 100 c. c. of benzene for three hours. After hydrogen chloride ceased to be evolved, the product was treated in the same way as the corresponding anilide derivative. It began to decompose at 120° and melted at 140° (Found : S = 25·28. $C_{11}H_{11}O_2NS_2$ requires S = 25·29 per cent.).

The *dinitro*-derivative was prepared in the same way as the corresponding dinitroanilide, and obtained as a yellow powder decomposing at 170° (Found: N = 12·16; S = 18·85. $C_{11}H_9O_6N_3S_2$ requires N = 12·24; S = 18·65 per cent.).

Acetoacet-o-*toluidide*.—This substance was prepared in the same way as the corresponding *p*-tolyl derivative, and after recrystallisation from benzene and petroleum melted at 107°. It is very soluble in alcohol or benzene and sparingly soluble in ligroin (Found: N = 7·62. $C_{11}H_{13}O_2N$ requires N = 7·33 per cent.).

Dithioacetoacet-o-*toluidide*.—The *o*-toluidide was treated with sulphur monochloride in the same way and in the same proportions as the corresponding para-derivative. The product, on repeated purification from a mixture of benzene and petroleum, melted and decomposed at 167° (Found: S = 25·26. $C_{11}H_{11}O_2NS_2$ requires S = 25·29 per cent.).

We take this opportunity to record our thanks to the Chemical Society for a grant which has partly defrayed the expense of this investigation.

The Baroda College, Baroda, India.

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V.—Absorption of Halogens by Mercurous Salts: Preliminary Note.—The present work grew out of an attempt to make a more effective mercurial preparation for external application by treating calomel with iodine. In spite of the large amount of work which has been done on various complex mercuric compounds,[1] the mixed mercuric salts, X—Hg—Y, have not been prepared by the action of halogens on mercurous compounds. During the present study, mercurous chloride, sulfate, and nitrate have been treated with alcoholic solutions of iodine and bromine in excess. Mercurous chloride yields mercuric iodochloride, HgICl, and mercuric bromochloride, HgBrCl. The sulfate yields diiodomercuric sulfate, $(IHg)_2SO_4$, and a perbromide, $(BrHg)_2SO_4.Br_2$. The latter compound reacts with dry chlorine to give dichloromercuric sulfate, $(ClHg)_2SO_4$. The nitrate gives a per-iodide, $(IHgNO_3)_2.I_2$, and a perbromide, $(BrHgNO_3)_2.Br_2$. The former compound, when treated with chlorine, differs from the corresponding sulfate by giving a perchloride, $(ClHgNO_3)_2.Cl_2$.

It is too early to discuss definitely the constitution of this series of compounds of mercury. They exhibit a number of interesting peculiarities which are being actively studied by physicochemical means. The study of their therapeutic effects may lead to interesting developments. As they contain easily reactive halogen atoms, they might be useful in making other compounds of mercury or in organic synthesis.

The experimental details of the preparation and properties of the substances, as well as the analytical data, will be published in a later paper on their constitution.

1 Ditte, *Compt. rend*, 87, 794 (1879); 92, 353 (1881). Varet, *ibid.*, 123, 497 (1896). Harth, *Z. anorg. Chem.*, 14, 323 (1897). Dobrosserdoff, *J. Russ. Phys. Chem. Soc*, 33, 303, 387 (1901) Sherrill, *Z. physic. Chem.*, 43, 705 (1903). Borelli, *Gazz. chim. ital*, 38, I, 361 (1908); 38, II, 421 (1908).

The Chemical Laboratories of the College Baroda, India

Kuverji Gosai Naik, Mahadeo Dattatraya Avasare.

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VI—Interaction of Sulphur Monochloride with Organic Acid Amides. Part II

By Kuverji Gosai Naik and Chaturbhai Shankarbhai Patel.

It is well-known that dry gaseous ammonia interacts vigorously with sulphur monochloride with the precipitation of sulphur (Naik, T., 1921, **119** 1166). In a previous communication (*loc. cit.*), it was shown that when this ammoniacal reactivity was neutralised by strong acid residues, *e. g.*, in the organic acid amides such as oxamide, malonamide, succinamide, phthalamide, etc., sulphur monochloride reacts no longer. Between these two extreme limits, of vigorous reactivity and no reactivity, come a number of cases where the reactivity of the amido group is only partially neutralised by the acid character of other residue.

The amides of acetic and benzoic acids interact with sulphur monochloride giving a mono-sulphide (*loc. cit.*), which is presumably derived from a disulphide, $\left.\begin{matrix}-NH\\-NH\end{matrix}\right\}S=S$, that had been initially formed.

The work described in this paper was undertaken with a view to throw some additional light on the condttions governing the reactivity of the amido group in organic acid amides, and also on those which govern the stability of the sulphur atom present in the resulting monosulphides. By weakening the acid residue of the amides still further, the reactivity of the amido group may be slowly increased, a point being ultimately reached where it is possible that the monosulphide would change into a condensed di-imido or hydrazine, $\begin{matrix}-NH\\|\\-NH\end{matrix}$ derivative, a limit, which, if achieved, would correspond to a stage just below the extreme one, *viz.*, when dry ammonia interacts with sulphur monochloride.

With the above end in view, isobutyramide, valeramide, and capronamide were selected. The reaction with sulphur monochloride in all the three cases followed a very simple course, two molecules of the amide condensing to give a di-amide with profuse evolution of all the sulphur, thus :

$$\left.\begin{array}{l|c|}CH_3{\cdot}(CH_2)_3{\cdot}CONH & H \quad Cl \\ & + \\ CH_3{\cdot}(CH_2)_3{\cdot}CONH & H \quad Cl\end{array}\right\} S=S \longrightarrow$$

$$(CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CONH)_2 + 2HCl + 2S \qquad (I)$$

and so on for the others.

These products which showed no trace of sulphur usually had showed higher melting points than the original amides from which they were found to be different by the method of mixed melting points. The molecular weights, too, when determined by the cryoscopic method, gave results in complete accord with those required for the condensed product. Moreover, the di-imido product obtained from capronamide, gave the original amide, on reduction with alcoholic sodium hydrosulphide, thus proving its constitution.

The effect of strengthening the acid group on the reactivity of the amido group, was also studied by selecting monochloracetamide and trichloracetamide as typical examples. Whereas the ammoniacal reactivity of the amido group in acetamide and monochloracetamide was sufficient to give a mono-sulphide, that in trichloracetamide was reduced to the desired extent and gave the expected di-imido product, thus :

$$\left.\begin{array}{l|c|}ClCH_2{\cdot}CONH & H \quad Cl \\ & + \\ ClCH_2{\cdot}CONH & H \quad Cl\end{array}\right\} S=S \longrightarrow (ClCH_2CONH)_2S + 2HCl + S. \quad (II)$$

$$\left.\begin{array}{l|c|}Cl_3C{\cdot}CO{\cdot}NH & H \quad Cl \\ & + \\ Cl_3C{\cdot}CO{\cdot}NH & H \quad Cl\end{array}\right\} S=S \longrightarrow \begin{array}{c}Cl_3C{\cdot}CONH \\ | \\ Cl_3C{\cdot}CONH\end{array} + 2HCl + 2S. \qquad (III)$$

Experiments were also instituted with a view to examine the possibilities of transferring the activity from the amido group in CH_3CONH_2 to the methylene group by substituting one of the hydrogen atoms of the methyl group by acidic groups such as phenyl and cyanogen (*cf.* Naik, T., 1921, **119**, 379). The reaction with phenylacetamide was inconclusive, and is being investigated more thoroughly, whilst in the case of cyanacetamide the reactivity was found to be transferred from the amido to the methylene group, thus :

$$\begin{array}{c}\left.\begin{array}{r}CN\\NH_2CO\end{array}\right\}CH_2\\ \left.\begin{array}{r}NH_2CO\\CN\end{array}\right\}CH_2\end{array} + \left.\begin{array}{r}Cl\\Cl\end{array}\right\}S{=}S \longrightarrow \left.\begin{array}{l}\left.\begin{array}{r}CN\\NH_2CO\end{array}\right\}CH\\ \left.\begin{array}{r}NH_2CO\\CN\end{array}\right\}CH\end{array}\right\}S{=}S. \qquad (IV)$$

The reaction was very vigorous, as was the case with cyanacetic ester (Naik, T., 1921, **119**, 1232).

Further, the reactions of sulphur monochloride with substituted amides such as isobutyranilide, phenylacetanilide, and acetylsalicylanilide were studied. Whereas isobutyranilide and phenylacetanilide gave a disulphide, thus resembling the reaction of salicylamide, (*loc. cit.*) :

$$2(CH_3)_2CHCONHC_6H_5 + S_2Cl_2 \longrightarrow \qquad (V)$$
$$(CH_3)_2CHCONHC_6H_4{-}S{-}S{-}C_6H_4NHCOCH(CH_3)_2$$

$$2C_6H_5CH_2CONHC_6H_5 + S_2Cl_2 \longrightarrow$$
$$C_6H_5CH_2CONHC_6H_4{-}S{-}S{-}C_6H_4NHCOCH_2C_6H_5, \qquad (VI)$$

acetylsalicylanilide gave a trisulphide, resembling the reactions of acetanilide and benzanilide with sulphur monochloride :

$$2\left.\begin{array}{l}CH_3\cdot CO\cdot O\\C_6H_5NHCO\end{array}\right\}C_6H_4 + S_2Cl_2 \longrightarrow$$
$$\left.\begin{array}{r}CH_3CO\cdot O\\C_6H_5NHCO\end{array}\right\}C_6H_3{-}S{-}S{-}S{-}C_6H_3\left\{\begin{array}{l}O\cdot CO\cdot CH_3\\CONHC_6H_5\end{array}\right. \qquad (VII)$$

On nitration of the disulphide resulting from (VI), a tetranitroderivative was obtained as before (*loc. cit.*).

Experimental.

Symm-dicaproyl hydrazine

Capronamide (3 grams) and sulphur monochloride (2 grams) were separately dissolved in dry petroleum (25 c. c. for each) and boiled under a reflux condenser. The reaction started with evolution of hydrogen chloride. After three hours the flask was allowed to cool and a viscous mass deposited at the bottom. The excess of sulphur monochloride was washed away with dry petroleum and the product was kept overnight in vacuum in an alkali desiccator. On being boiled with animal charcoal in benzene and filtered, it deposited from the clear filtrate on cooling, in plates with pearly lustre, and melted on recrystallisation at 111—112°C. The original amide melted at 98°C, while the mixture of the two melted at 95°C. It was easily soluble in benzene, alcohol, acetone and warm water, more difficultly soluble in chloroform, insoluble in petroleum and carbon disulphide.

Molecular Complexity.—A specimen recrystallised from benzene and carefully dried gave the following molecular complextty by the cryoscopic method in this solvent; 0.0102 grams and 0.0152 grams dissolved in 20 c. c. of benzene depressed the freezing point by 0.011°C and 0.019°C, respectively; M = 265, 229 (average 247). $C_{12}H_{24}O_2N_2$ requires M = 228. (Found: N = 12.39. $C_{12}H_{24}O_2N_2$ requires N = 12.28 per cent). There was no sulphur in the compound.

Reduction.—5 grams of the above compound were dissolved in 50 c. c. of absolute alcohol and an aqueous solution of sodium hydrosulphide and caustic soda was gradually added (Brand, Ber., 1906, **42**, 3464). On cooling a crystalline precipitate was obtained. The crystals were washed free from alkali with hot water and the product on recrystallisation from alcohol melted at 98°C. It was found to be pure capronamide.

Symm-divaleryl hydrazine.

Valeramide (3 grams) and sulphur monochloride (2·5 grams) were separately dissolved in dry petroleum (15 c. c. in each case), mixed and boiled. Hydrogen chloride began to evolve on heating this mixture. The brown viscous solid deposited on completion of reaction (3 hours), gave shining pearly plates from benzene, as in the case of capronamide, which melted at 123°C. It was soluble in benzene, alcohol, acetone and also in warm water, but insoluble in petroleum and carbon bisulphide.

Molecular Complexity.—0·0194 gram of the substance dissolved in 20 c. c. of benzene depressed the freezing point by 0·025°C; M = 222. $C_{10}H_{20}N_2O_2$ requires M = 200. (Found: N = 14·25. $C_{10}H_{20}O_2N_2$ requires N = 14·00 per cent.). Sulphur was found to be absent.

Symm-di-isobutyryl hydrazine.

Isobutyramide (3 grams) and sulphur monochloride (3 grams) dissolved in dry petroleum (50 c. c.) were boiled under a reflux condenser. Copious evolution of hydrogen chloride was observed. After treatment of the brown viscous residue in the same way as before, pearly white plates melting at 120—121°C were obtained. The product was found to be easily soluble in benzene, alcohol and acetone, but only slightly soluble in chloroform.

Molecular Complexity.—0·0088 grams of the substance dissolved in 20 c. c of benzene depressed the freezing point by 0·014°C. M = 180. $C_8H_{16}O_2N_2$ requires M = 172. (Found: N = 16·20. $C_8H_{16}O_2N_2$ requires N = 16·28 per cent.). The compound contained no sulphur.

N-sulphidolies-chloracetamide,

A mixture of monochloracetamide (3 grams) and sulphur monochloride (3 grams) in 50 c. c. of dry benzene was boiled

till the evolution of hydrogen chloride ceased. A white solid was gradually deposited. The reaction was stopped after 6 hours, the product filtered, washed free from sulphur monochloride and crystallised from hot alcohol, when it was obtained in shining white crystals. It begins to melt at 165°C (decomp.), forming a yellow liquid. (Found : N = 13·14; S = 14·5; Cl = 32·26. $C_4H_6O_2N_2Cl_2S$ requires N = 12·90; S = 14·75 and Cl = 32·72 per cent.).

Symm-hexachlordiacetyl hydrazine.

Trichloracetamide (6 grams) and sulphur monochloride (2 grams) were boiled in dry benzene (50 c. c.) as in the previous case. A brisk evolution of hydrogen chloride was noted. On cooling a yellowish white mass was deposited which on being freed from the excess of sulphur monochloride and sulphur, was crystallised from benzene and obtained in the form of white needles. On recrystallisation from benzene it melted at 148—149°C. Trichloracetamide melts at 140°C.

Molecular Complexity.—0·0423 grams of the substance dissolved in 20 c. c. of benzene depressed the freezing point by 0·035°C. M = 338. $C_4H_2O_2N_2Cl_6$ requires M = 323. (Found: N = 8·80; Cl = 65·80. $C_4H_2O_2N_2Cl_6$ requires N = 8·67 and Cl = 65·94 per cent.). No sulphur was detected in this compound.

Cyanacetamide-C-disulphide.

Cyanacetamide (3 grams) and sulphur monochloride (3 grams) were boiled in dry benzene (50 c. c.). A brown granular mass was obtained as the evolution of hydrogen chloride proceeded quickly. On completion of the reaction (after 4 hours), the excess of sulphur monochloride was removed by hot benzene. The product was freed from sulphur by being repeatedly boiled under a reflux condenser with carbon disulphide until the melting point became constant. It melts at 103°C (decomp.); it is insoluble in

benzene, petroleum and carbon disulphide, and hydrolyses in alcohol. On standing it undergoes slow decomposition to a dark mass. (Found: N = 24.77; S = 27.73. $C_6H_6O_2N_4S_2$ requires N = 24.34 and S = 27.82 per cent).

Symm-di-isobutyryl-diamino-diphenyl disulphide.

Isobutyranilide (3 grams) and sulphur monochloride (3 grams) were boiled together in dry benzene (50 c. c.) for 12 hours. The resulting pink coloured solution was slowly evaporated in a current of dry hot air, when an indigo coloured mass was obtained. On boiling in benzene with animal charcoal and leaving the solid mass obtained on evaporation of the solvent benzene, in an alkaline desiccator, it was freed from the hydrogen chloride with which it was at first contaminated. The resulting granular mass was redissolved in benzene from which it was deposited in the form of an indigo coloured amorphous granular powder melting at 100—102°C (decomp.), very easily soluble in benzene forming a beautiful violet coloured solution and also soluble in alcohol and acetone. (Found : N = 7.55; S = 16.9. $C_{20}H_{24}O_2N_2S_2$ requires N = 7.22 and S = 16.5 per cent.).

Symm-diphenyl-diacetyl-diamino-diphenyl-disulphide.

Equal quantities (5 grams) of phenylacetanilide and sulphur monochloride were boiled together in dry benzene (50 c. c.) for 15 hours. The excess of sulphur monochloride was then evaporated in a draught of dry air, the viscous solid residue redissolved in benzene and precipitated by petroleum. It melted at 162 to 163°C. (Found : N = 5.68, S = 12.98. $C_{28}H_{24}O_2N_2S_2$ requires N = 5.79 and S = 13.22 per cent.).

Symm-tetranitro-diphenyl-diacetyl-diamino-diphenyl-disulphide.

Two grams of the above substance were gradually treated with 10 c. c. fuming nitric acid (S. G. 1.5), keeping the

temperature low. At first a sudden evolution of the oxides of nitrogen took place, the disulphide going into solution at the same time. The liquid was slightly concentrated, allowed to cool and filtered, when on slight dilution with water, a very pure yellowish mass was obtained, which melted at 148—150°C (decomp). (Found : N=12.76; S=9.23. $C_{28}H_{20}O_{10}N_6S_2$ requires N=12.65 and S=9.64 per cent.).

Symm-diacetoxy-dianilino-diformyl-diphenyl-trisulphide.

Acetylsalicylanilide (4 grams) were boiled in dry benzene (100 c. c.) with sulphur monochloride (3 grams) for eighteen hours. After the evaporation of the solution in a current of dry air, the dirty white viscous mass obtained was redissolved in benzene and boiled with animal charcoal. The clear filtrate was allowed to drop into a large quantity of petroleum ether, when a partly granular and partly viscous mass was obtained. This was left in an alkaline desiccator overnight, dissolved in benzene and precipitated by petroleum in the form of a light yellow powder which melted at 78°C (decomp.), (Found: S=15.62. $C_{30}H_{24}O_6N_2S_3$ requires S=15.89 per cent.).

The Chemical Laboratories,
The Baroda College,

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VII—*Absorption of the Halogens by Mercurous Salts Part 1.*

Formation and Properties of some Complex Compounds of Mercury.

BY KUVERJI GOSAI NAIK AND MAHADEO DATTATRAYA AVASARE.

The work undertaken (a preliminary note on which appeared in J. Amer. C. S., Vol. 45 (notes), pp. 2769-70) originated during the course of a mercurial preparation involving the use of calomel for outside application in which it was thought advisable to use iodine, as it was expected that (1) calomel would combine with iodine to form a compound with increased mercurial activity and (2) the iodine being a germicide would contribute favourably to the germicidal properties of the preparation.

The toxicity of mercuric salts is directly related to the ionising capacity of the salts, whilst mercurous salts like calomel, which are insoluble, cannot be absorbed to the necessary extent, and so their use as germicides is limited. It appeared, therefore, that if some way could be found to slightly increase the solubility of these compounds, without very much increasing their degree of dissociation, their usefulness would be greatly enhanced.

In the work described here the mercurous salts, chloride, sulphate and nitrate were shaken with alcoholic solutions of bromine and iodine. The latter were rapidly absorbed and gave beautiful crystalline compounds from which attempts were made to produce the corresponding chloro-derivatives by passing dry chlorine gas over them. During the course of this work the following compounds were obtained :—

From mercurous chloride—

Iodine	Bromine	Chlorine
(1) $Hg<^{Cl}_{I}$	(2) $Hg<^{Cl}_{Br}$	(3) $Hg<^{Cl}_{Cl}$

From mercurous sulphate—

(4) $SO_4{<}\begin{matrix}Hg\text{-}I\\ Hg\text{-}I\end{matrix}$ (5) $\left[SO_4{<}\begin{matrix}Hg\text{-}Br\\ Hg\text{-}Br\end{matrix}\right]Br_2$ (6) $SO_4{<}\begin{matrix}Hg\text{-}Cl\\ Hg\text{-}Cl\end{matrix}$

From mercurous nitrate—

(7) $\left[Hg{<}\begin{matrix}No_3\\ I\end{matrix}\right]_2 I_2$ (8) $\left[Hg{<}\begin{matrix}No_3\\ Br\end{matrix}\right]_2 Br_2$ (9) $\left[Hg{<}\begin{matrix}No_3\\ Cl\end{matrix}\right]_2 Cl_2$

Compound (1) has been prepared by Kohler (B. *12*, 1187) and by others but in small yield, whilst the method described here is extremely simple and gives quantitative yields of the pure product.

The fact that compound (5) was soluble in boiling water and it was found possible to estimate its bromine quantitatively in the ordinary way as silver bromide from its aqueous solution, as well as the fact that (6), which is derived from (5) by passing chlorine gas over it, is also soluble in water and in which chlorine could be estimated in the usual way, excludes the possibility of such compounds being molecular compounds or double salts having the formulæ $HgSO_4.Hg\,Br_2.Br_2$ and $HgSO_4{\cdot}HgCl_2$. For it is well known that under such circumstances mercuric sulphate (and mercuric nitrate as well) would hydrolyse to a basic mercuric salt which will precipitate as a yellow substance. Hence the mercury atom in such compounds can be suggested to form a part of the molecular complex, which would perhaps render such a preparation therapeutically useful.

The interaction of mercurous nitrate with the halogens gave tetrahalogen derivatives (7), (8) and (9). The bromo- and the chloro- derivatives (8) and (9), like (5), were soluble in a large quantity of boiling water without any hydrolysis and it was from the water solutions that the halogens were estimated in the usual way, confirming the view that all these compounds are not double salts but complex compounds.

EXPERIMENTAL

(1) *Mercuric Chloriodide.*

Two grams of powdered calomel were shaken with an alcoholic solution of iodine in a stoppered bottle at room temperature. The iodine began to be rapidly absorbed. After the absorption of the iodine ceased, the solution was kept for some days and a beautiful red crystalline compound was obtained. It was re-crystallised from alcohol. It changed from red to yellow at 125° and melted to a yellow liquid at 153°. Yield three grams.

(Found: Cl=9·58; I=35·22. HgClI requires Cl=9·79; I=35·03 per cent.)

The compound, though insoluble in water, dissolved readily in alcohol.

(2) *Mercuricchlorbromide*

Four grams of finely powdered calomel were shaken with an alcoholic solution of bromine as before, when the bromine was found to be rapidly absorbed with rise of temperature. The reaction mixture was consequently kept at room temperature by slightly cooling it under the tap. When bromine ceased to be absorbed, the solution was allowed to evaporate to remove the excess of bromine, when a syrupy liquid was obtained which yielded a white crystalline mass on standing over sulphuric acid in a desiccator. It slowly sublimes without melting, when heated in a melting point tube. (Found: Cl=11·23; Br=24·98. HgClBr requires Cl=11·26; Br=25·36 per cent.)

The compound was freely soluble in alcohol, sparingly soluble in cold water, easily soluble in boiling water.

When its solution in water is treated with silver nitrate, silver bromide is quantitatively precipitated.

On passing dry chlorine over mercuric chloriodide (1), at room temperature in a tube open at both ends, and driving away the excess chlorine by means of dry carbon dioxide, a white mass was obtained which when crystallised from alcohol was found to be identical with mercuric chloride ($HgCl_2$).

(4) *Di-iodo-dimercuric sulphate*

This compound was obtained as a red crystalline mass by shaking mercurous sulphate with an alcoholic solution of iodine under the conditions stated above. When crystallised from alcohol it turned yellow at 143° and melted at 243° Yield quantitative.

(Found: I = 33·87. $Hg_2SO_4I_2$ requires I = 33·86 per cent.).

The compound though insoluble in water was soluble in alcohol.

(5) *Tetrabromodimercuric sulphate.*

On treating mercurous sulphate with an alcoholic solution of bromine, under the conditions already described, a syrupy liquid was obtained, which deposited a white crystalline mass when left to crystallise in a desiccator over sulphuric acid. On recrystallisation from alcohol, it was found to decompose at 125° and melt with decomposition at 235°.

(Found: Br = 39·17; Hg = 49·10; SO_4 = 11·78. $Hg_2SO_4Br_4$ requires Br = 39·21; Hg = 49·03; SO_4 = 11·77 per cent.).

The compound was found to be sparingly soluble in cold water, more in boiling water. It dissolved freely in alcohol. When allowed to stand in air it slowly emitted vapours of bromine. Silver bromide was quantitatively precipitated from its solution in water by the addition of silver nitrate.

(6) *Di-chlorodimercuricsulphate.*

When dry chlorine gas was passed over (5) tetrabromodimercuric sulphate, a white amorphous mass was obtained which when crystallised from alcohol began to darken at 175° and melted at 270°.

(Found : Cl = 12.50. $Hg_2SO_4Cl_2$ requires Cl = 12.52 per cent.).

It is sparingly soluble in cold water, more in hot water and freely soluble in alcohol. Its halogen was estimated in the usual way from its water solution.

(7) *Tetraiododimercurionitrate*

Mercurous nitrate was shaken with an alcoholic solution of iodine, as before. The resulting red compound was crystallised from alcohol, when it changed to yellow at 145-146° and melted at 250°. Yield quantitative.

(Found : I = 49.22. $Hg_2(NO_3)_2I_4$ requires I = 49.23 per cent.).

(8) *Tetrabromodimercuricnitrate.*

This compound was prepared in the same way, as its corresponding iodo derivative, using an alcoholic solution of bromine in place of iodine. The resulting liquid, after the excess of bromine was allowed to go away, gave on standing over sulphuric acid in a desiccator, a white crystalline substance which on subseqent re-crystallisation from alcohol, yielded a compound which decomposed on heating.

(Found : Br = 38.02. $Hg_2(NO_3)_2Br_4$ requires Br = 37.91 per cent.)

The compound was very soluble in alcohol, appreciably soluble in cold water and more in hot water without decomposition. The halogen was estimated in the usual way from its water solution.

(9) *Tetrachlorodimercuricnitrate.*

The above compound was obtained as a white amorphous powder, when dry chlorine gas was passed over (7) the corresponding tetraiodo compound. On crystallisation from alcohol it begins to decompose and darken at 100°. Yield quantitative.

(Found : $Cl=21{\cdot}16$. $Hg_2(NO_3)_2Cl_4$ requires $Cl=21{\cdot}32$ per cent).

The compound was sparingly soluble in cold water, more in boiling water and freely soluble in alcohol. The halogen could be quantitatively precipitated from its water solution by silver nitrate.

The Chemistry Department of the College,
Baroda, India.

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VIII.—Interaction of Sulphur Dichloride with Substances containing the Reactive Methylene ($-CH_2-$) Group or Substituted Methylene Group.

By Kuverji Gosai Naik and Ganpat Vishram Jadhav.

The work was undertaken with a view (1) to study the reactivity of the hydrogen atoms of a methylene group situated between two carbonyl groups as in the case of substituted amides of malonic and methylmalonic acid, and (2) to throw light on the debated and vexed question of the constitution of sulphur dichloride.

The existence of a definite compound of the composition, SCl_2 has been repeatedly called in question (J. *Chem. Soc.*, 1870, *23*, 455, 1871, *24*, 1163, *Compt. rend.* 1878, *86*, 664; *Bul. Soc. Chim.*, 1886, *45*, 867). SCl_2 has been regarded by some as a solution of chlorine in sulphur monochloride and by others as a compound in the state of partial dissociation. Costa (*Gazzetta*, 1890, *20*, 367) determined cryoscopically the molecular weight of the reddish brown liquid obtained by saturating the monochloride with chlorine below 0° and then removing the excess of chlorine by a current of carbon dioxide. The results of the determinations of molecular weight in benzene and in acetic acid solutions agree with the formula SCl_2. This view was challenged by Ruff and Fischer (*Ber.*, 1903, *36*, 418) who assert that they got no evidence of

the existence of the compound SCl_2 when they examined the composition of the liquid and the vapours at temperatures between —10°C and 0°. Böeseken (*Rec. trav. chim.*, 1905, *24*, 209) obtained diphenyl sulphide by the interaction of sulphur dichloride with benzene in the presence of anhydrous aluminium chloride at 0°. This supports the view that at low temperatures sulphur dichloride possesses the formula SCl_2. At 60°, however, the reaction takes a different course, chlorobenzene and thianthrene being the products formed. This is attributed to the decomposition of sulphur dichloride into the monochloride and chlorine, the latter then attacking the benzene nucleus.

Beckmann and his collaborators (*Zeit. physikal. Chem.*, 1909, *65*, 289) determined the molecular weights of the monochloride and the dichloride. They found that in liquid chlorine, at its boiling point, sulphur monochloride and sulphur dichloride have the molecular weights corresponding to the formulæ S_2Cl_2 and SCl_2 respectively. They also arrived at the formula SCl_2 by means of cryoscopic determinations in xylene, *p*-xylene, ethylene dibromide, acetic acid and bromine solution. These results seem to have been confirmed by the work of Bergmann and Bloch (*Ber.*, 1920, *53*, [**B**], 977).

Malonanilide and malon di-*o*-tolylamide interact with SCl_2 as follows :—

$$\begin{matrix} RNH{\cdot}CO \\ RNH{\cdot}CO \end{matrix}{>}CH_2 + 2SCl_2 \longrightarrow \begin{matrix} RNHCO \\ RNHCO \end{matrix}{>}C{<}\begin{matrix} S{-}Cl \\ S{-}Cl \end{matrix} + 2HCl \quad (1)$$

where R stands for the phenyl or the tolyl group.

In the case of both methyl-malonanilide and methyl-malon di-*o*-tolylamide only one hydrogen atom in the reactive $—CH_2—$ group is available for interaction with sulphur dichloride, thus :—

$$\begin{matrix} RNH{\cdot}CO & & H \\ & >C< & \\ RNH{\cdot}CO & & CH_3 \end{matrix} + SCl_2 \longrightarrow \begin{matrix} RNHCO & & S{-}Cl \\ & >C< & \\ RNHCO & & CH_3 \end{matrix} + HCl \quad (II)$$

where R represents either the phenyl or the tolyl group.

From the above it will be evident that the total negativity of the adjoining group, ·CO·NHR (where R is either phenyl or tolyl) which influences the reactivity of the hydrogens of the methylene group is practically the same, and hence the reaction should follow the same course. Experiments have justified this.

It also appears that both the hydrogens of the methylene group in compound (I) are simultaneously attacked by sulphur dichloride. This is in contrast with what happens in the case of sulphur monochloride, where one molecule of the substituted amide reacts with one molecule of sulphur monochloride and not two (Naik, *J. Chem. Soc.*, 1921, *119*, 379). Thus in the case of sulphur monochloride the reaction follows the course :—

$$\begin{matrix} RNHCO & & H \\ & >C< & \\ RNHCO & & H \end{matrix} + \begin{matrix} Cl\,S \\ | \\ Cl\,S \end{matrix} \longrightarrow \begin{matrix} RNHCO & & S \\ & >C< & | \\ RNHCO & & S \end{matrix} + 2HCl \qquad (III)$$

where R is either the phenyl or tolyl group.

It is interesting to observe that, in general, the dithioketones obtained by the interaction of sulphur monochloride with some of the substituted amides are extremely stable (Naik, *J. Chem. Soc.*, 1921, *119*, 1231), whereas the compounds obtained by the action of sulphur dichloride are unstable, when treated with fuming nitric acid. In the case of compound (I) the reaction proceeds as follows :—

$$\begin{matrix} RNHCO & & S{-}Cl \\ & >C< & \\ RNHCO & & S{-}Cl \end{matrix} \xrightarrow{\text{nitration}} \begin{matrix} R_1(NO_2)NHCO & \\ & >CH_2 \\ R_1(NO_2)NHCO & \end{matrix}$$

where R_1 stands for phenylene or tolylene group.

The products obtained from malon di-*n*-propylamide and malon di-naphthylamides (α— and β—) belong to the same class. The reaction follows the course given below :—

$$\begin{array}{l}R_1NHCO\\ R_1NHCO\end{array}\!>C<\!\begin{array}{l}H\\ H\end{array}+\underset{(IV)}{Cl—S—Cl}\longrightarrow\begin{array}{l}R_1NHCO\\ R_1NHCO\end{array}\!>C<\!\begin{array}{l}H\\ S—Cl\end{array}+HCl\ (IV)$$

where R_1 stands for propyl group.

$$\begin{array}{l}RNHCO\\ RNHCO\end{array}\!>C<\!\begin{array}{l}H\\ H\end{array}+Cl—S—Cl\longrightarrow\underset{(V)}{\begin{array}{l}RNHCO\\ RNHCO\end{array}\!>C<\!\begin{array}{l}H\\ S—Cl\end{array}}+HCl\ (V)$$

Where R stands for α- or β-naphthyl group.

Here the total negativity of the group ·CO·NHR (where R is the propyl or naphthyl group) is reduced to a level which admits of the reactivity of only one of the hydrogens of the methylene group. In such cases it is but natural to expect the above course of the reaction.

These compounds are also unstable and lose all their sulphur and chlorine when nitrated, thus :—

$$\begin{array}{l}RNHCO\\ RNHCO\end{array}\!>C<\!\begin{array}{l}H\\ S—Cl\end{array}\xrightarrow{\text{Nitration}}\begin{array}{l}R_1(NO_2)\\ R_1(NO_2)\end{array}\!>CH_2$$

where R_1 stands for naphthylene group.

Finally, in the cases of malon di-*p*-tolylamide, malon di-benzylamide and methyl-malon-di-*p*-tolylamide the reaction with sulphur dichloride proceeds further and very unstable compounds containing excess of chlorine are produced. In the case of methyl-malon-di-*p*-tolylamide the methyl group also is attacked, thus :—

$$\begin{array}{l}RNHCO\\ RNHCO\end{array}\!>C<\!\begin{array}{l}H\\ H\end{array}+2SCl_2=\begin{array}{l}RNHCO\\ RNHCO\end{array}\!>C<\!\begin{array}{l}Cl\\ SCl\end{array}+2HCl+S\ (VI)$$

where R is a *p*-tolyl or benzyl group.

$$\begin{array}{l}C_7H_7NHCO\\ C_7H_7NHCO\end{array}\!>C<\!\begin{array}{l}CH_3\\ H\end{array}+2SCl_2=\begin{array}{l}C_7H_7NHCO\\ C_7H_7NHCO\end{array}\!>C<\!\begin{array}{c}CH_2\\ |\\ S\\ \wedge\\ Cl\ \ Cl\end{array}+2HCl$$

(VII)

The above products are stable only in a desiccator over sulphuric acid. In moist air they decompose, the original amide being obtained, with the evolution of hydrogen chloride and deposition of sulphur. It is interesting to observe that the tolyl compound (VI) on nitration loses all its sulphur and chlorine forming

$$[(NO_2)C_7H_6NH{\cdot}CO]_2CH_2$$

The constitutions assigned to the above compounds follow from the following considerations :—

(1) That the hydrogen atom or atoms attacked by the dichloride are not those from the aromatic nuclei is evident from the course of the reaction in case (IV) where no such aromatic nuclei are present.

(2) The two hydrogen atoms eliminated are not those which were originally attached to the two nitrogen atoms; because, if that was so, the course of the reaction in every case ought to have been the same, for every one of the amides has two available $\cdot CO{\cdot}NHR$ groups.

(3) On reduction with alkaline hydrosulphide, say, in the case of (I), the original amide is obtained,

$$(ClS)_2C: (CONHC_7H_7)_2 + 4H_2 = CH_2(CONHC_7H_7)_2 + 2HCl + 2H_2S$$

(4) That the original amide is obtained in the case of (VI) and (VII) in the presence of even a trace of moisture is sufficient to show that the reaction takes place with the hydrogens of the methylene group; because, if the interaction had taken place with the hydrogens of the aromatic nucleus, the substituted halogens could not be easily removed with water.

Apart from the light which the study of these reactions throws on the reactivity of the group, $CO{\cdot}CH_2{\cdot}CO$, another and a very important bearing of this work is in relation to the constitution of sulphur dichloride. The previous work done by one of us (Naik, *loc. cit.*) has tentatively* shown that sulphur monochloride reacts in two forms :

$$\begin{array}{l} Cl{-}S \\ \quad | \\ Cl{-}S \end{array} \qquad (I) \qquad\qquad S{=}S{<}\begin{array}{l} Cl \\ Cl \end{array} \qquad (II)$$

and it is only in the case of (I) that stable disulphides are obtained. It was suggested in the beginning that sulphur dichloride is a mixture of monochloride and chlorine, or of tetrachloride and monochloride (*Ber.*, 1903, *36*, 418). If this had been the case, in none of the above reactions could there have been a possibility of obtaining a definite class of compounds. The monochloride which was supposed to be one of the constituents which go to form the dichloride, ought to have contributed stable dithioketones, as was found out by Naik (*loc. cit.*). The other constituent of sulphur dichloride, *viz.*, chlorine ought to have easily chlorinated the aromatic nucleus, and given aromatic chloro-compounds. But in no case were nuclei substituted halogen derivatives obtained. On the other hand, the compounds obtained possessed a separate identity of their own. It is, therefore, beyond doubt that sulphur dichloride did neither react as a mixture of sulphur tetrachloride and monochloride, but it is a definite chloride of sulphur having the formula SCl_2.

EXPERIMENTAL.

The reactions were carried out in benzene solution. Under the conditions of the experiments there was no interaction between the solvent and the sulphur dichloride. In most cases the product of reaction separated from the cold solution in the crystalline form. Dry materials were always used, and when a reaction mixture had to be left overnight, precautions were taken against the entrance of moisture.

Sulphur Dichloride and Malon-anilide

Malon anilide (3 g.) was mixed with dry benzene (20 c.c.), and sulphur dichloride (6g.) was added to the mixture. The reaction started at once and hydrochloric acid gas was evolved. The flask was corked with calcium chloride tube

to avoid moisture and was left overnight. Next day it was heated under reflux over a sand-bath for four hours. As soon as benzene began to boil, copious fumes of hydrochloric acid gas were thrown out. The clear solution on standing deposited feathery needle-shaped crystals. They were filtered and washed with dry petroleum. They were found to be very soluble in acetic acid, fairly soluble in alcohol, benzene and chloroform, sparingly soluble in light petroleum. On crystallisation from benzene the substance melted at 164-165°. (Found: Cl=18·69; S=16·72. $C_{16}H_{12}N_2O_2S_2Cl_2$ requires Cl=18·35; S=16·54 per cent.).

Nitration.—The compound (1 g.) was gradually added to fuming nitric acid (7 c.c.). Nitrogen peroxide came off and the mixture became hot. After some time air was blown into the acid to remove the fumes of nitrogen peroxide. The colourless liquid was then slowly added to water, when a yellow solid separated. It was filtered and washed completely with water. It shrank at 81° and melted with decomposition at 90°. (Found: N=16·10. $C_{16}H_{12}N_4O_6$ requires N=16·28 per cent.).

Sulphur Dichloride and Malon-di-o-tolylamide.

Malon-di-*o*-tolylamide (2 g.) was mixed with dry benzene (20 c.c.), and sulphur dichloride (5 g.) was added to the mixture. The reaction was vigorous and copious fumes of hydrogen chloride were formed. The mixture was refluxed over a sand-bath for three hours. On standing the clear liquid deposited white silky needles. They were filtered and washed with dry petroleum. They were soluble in benzene, alcohol, acetone, carbon tetrachloride and chloroform, and sparingly soluble in ether and petroleum. They were crystallised from hot benzene; m. p. 160-161°. (Found: Cl=17·34; S=15·55. $C_{17}H_{16}N_2O_2S_2Cl_2$ requires Cl=17·11; S=15·43 per cent.)

Reduction.—The substance (1 g.) was dissolved in alcohol, and 10 c. c. of an aqueous solution of sodium hydrogen

sulphide (A solution was made by saturating 1·5 g. of caustic soda with hydrogen sulphide in a small quantity of water. To it caustic soda (5·7 g.) dissolved in a small quantity of water was added and the whole made up to 30 c. c.) was gradually added to it, when a brown solution was obtained. The solution was diluted with water, and the solid obtained was washed with water. It was crystallised from glacial acetic acid; m. p. 190-191°. It contained neither chlorine nor sulphur and was identified as the original amide.

Nitration.—The compound (1 g.) was gradually added to 10 c. c. of fuming nitric acid when fumes of nitrogen peroxide were thrown out. The liquid, after sometime, was warmed a little on a water-bath. After blowing air through the acid, the nearly colourless liquid was diluted with water and the reddish mass obtained was filtered and washed with cold water. It shrank at 75° and melted with decomposition at 85°. (Found: N = 14·88. $C_{17}H_{19}O_6N_4$ requires N = 15·05 per cent.).

Sulphur Dichloride and Methyl-malonanilide.

Methyl malonanilide (2 g.) was added to dry benzene (15 c. c.), and sulphur dichloride (4 g.) was then added to it. The reaction mixture was finished up as in the preceding case. The solid was soluble in acetic acid, alcohol, acetone, benzene and chloroform, and sparingly soluble in ether and petroleum: m. p. 132°. (Found: Cl = 10·39; S = 9·27, $C_{16}H_{15}N_2O_2SCl$ requires Cl = 10·61; S = 9·56 per cent.).

Sulphur Dichloride and Methyl-malon-di-o-tolylamide.

Methyl-malon-di-o-tolylamide (2 g.) was put in 15 c. c. of dry benzene and sulphur dichloride (4 g.) was added to it. The reaction mixture was heated under reflux over a sand-bath for three hours, after keeping it at ordinary temperature for some time. On standing, same crystals

were deposited and more solid was obtained on dilution with dry petroleum. The mass was crystallised from benzene; m. p. 150° (Found : $Cl=9{\cdot}39$; $S=8{\cdot}69$ $C_{18}H_{19}N_2O_2SCl$ requires $Cl=9{\cdot}79$; $S=8{\cdot}82$ per cent.).

Sulphur Dichloride and Malon-di-α-naphthylamide.

Malon di-α-naphthylamide (3 g.) was added to 20 c. c. of dry benzene. Sulphur dichloride (7 g.) dissolved in a little benzene was then added to the mixture. After some time, the mixture was refluxed over a sand-bath for three hours when hydrogen chloride ceased to evolve. When benzene began to boil, the liquid assumed green colour. On standing the solution deposited a solid which was filtered and washed with dry petroleum. The white mass soon began to be blue on the surface. It was therefore put in a desiccator. It was crystallised from benzene. It became blue. It was soluble in acetic acid, acetone, benzene and carbon tetrachloride, and sparingly soluble in ether and petroleum. It melted with decomposition at 145°. (Found: $Cl=8{\cdot}63$; $S=8{\cdot}09$. $C_{23}H_{17}N_2O_2SCl$ requires $Cl=8{\cdot}44$; $S=7{\cdot}6$ per cent.).

Sulphur Dichloride and Malon-di-β-naphthylamide.

The amide (5 g.) was added to 50 c. c. of dry benzene and sulphur dichloride (10 g.) was added to it. Hydrogen chloride was at once thrown out. The mixture was refluxed over a sand-bath for four hours, but the product was insoluble in benzene. On cooling the solid was filtered and washed. It was sparingly soluble in alcohol, acetone and ether, and fairly soluble in boiling acetic acid, from which it came down as an amorphous yellowish powder. It melted with decomposition at 230°—31°. (Found: $Cl=8{\cdot}55$; $S=7{\cdot}37$. $C_{23}H_{17}N_2O_2SCl$ requires $Cl=8{\cdot}44$; $S=7{\cdot}61$ per cent.).

Nitration.—The compound (1 g.) was gradually added to 10 c. c. of fuming nitric acid. Copious fumes of nitrogen peroxide were thrown out. The mixture was heated on a

water-bath for some time and then air was blown into the hot mixture to remove the fumes. It was then diluted with cold water and the yellowish solid obtained was filtered and washed. It shrank at 175° and melted with decomposition at 185°. (Found: N = 12·45. $C_{26}H_{16}N_4O_6$ requires N = 12·6 per cent.).

*Sulphur Dichloride and Malon-di-*n*-propylamide.*

The amide (2 g.) was added to 25 c. c. of dry benzene and sulphur dichloride (4 g.) was then added to it. The reaction started at once and the reaction mixture became hot. The flask was corked with a calcium chloride tube and left overnight. Next day it was refluxed over a sand-bath for about an hour and then concentrated, when a solid was deposited. It was filtered and washed with dry petroleum. On slow evaporation of petroleum the white solid began to smell of hydrochloric acid and became pasty. It was then placed in a desiccator over caustic soda for several days. Afterwards it was crystallised from dry benzene and the solid was washed with a mixture of ether and petroleum. It is soluble in alcohol and benzene, and sparingly soluble in chloroform, ether and petroleum; m. p. 141—142°. (Found : Cl = 13·80; S = 12·50. $C_9H_{17}N_2O_2SCl$ requires Cl = 14·06; S = 12·67 per cent.).

*Sulphur Dichloride and Malon-di-*p*-tolylamide.*

The amide (4 g.) was mixed with 25 c. c. of dry benzene and sulphur dichloride (8 g.) was added to the mixture. The reaction started at once with the evolution of hydrogen chloride. The flask was corked with a calcium chloride tube and left overnight at room temperature. Next day it was refluxed over a sand-bath for about four hours. On cooling the clear solution deposited white crystals which were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, acetone, benzene, carbon disulphide and chloroform. The solid was crystal-

lised from benzene; m. p. 158°. (Found: Cl=18·16; S=8·78. $C_{17}H_{16}N_2O_2SCl_2$ requires Cl=18·54; S=8·35 per cent.).

The compound when put in ordinary air was found to smell of hydrochloric acid after some days. This went on for about two months, after which period the compound assumed a yellowish tint. It was insoluble in benzene and was crystallised from glacial acetic acid; m. p. 247°. It was found to contain neither sulphur nor chlorine and was identified as the original amide. The compound is stable when put in a desiccator over concentrated sulphuric acid.

Nitration :—The compound (1 g) was gradually added to 8 c.c. of fuming nitric acid. Fumes of nitrogen peroxide were thrown out when the substance was being added. After some time air was blown into the acid and the nearly colourless solution was diluted with water, when a yellow mass was obtained. It shrank at 85° and melted with decomposition at 120°. (Found: N=14·72. $C_{17}H_{16}N_4O_6$ requires N=15·05 per cent.).

Sulphur Dichloride and Malon-di-benzylamide.

The amide (3 g.) was taken with 25 c.c. of dry benzene and sulphur dichloride (6 g,) was added to the mixture. The reaction mixture was corked with a calcium chloride tube and left overnight at room temperature. Next day it was refluxed over a sand-bath for six hours when hydrogen chloride ceased to evolve. The clear solution on standing deposited white silky needle-shaped crystals. They were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, acetone, benzene and chloroform. The mass was crystallised from boiling benzene, m. p. 149—150°. (Found: Cl=18·26; S=8·82. $C_{17}H_{16}N_2O_2SCl_2$ requires Cl=18·54; S=8·35 per cent.).

This product also decomposed as in the case of malon di-*p*-tolylamide and the original amide was obtained in this case too.

Sulphur Dichloride and Methyl-malon-di-p-tolylamide.

The amide (4 g.) was put in 25 c.c. of dry benzene and sulphur dichloride (8 g.) was added to the mixture. The flask was corked with a calcium chloride tube and left overnight at room temperature. Next day it was refluxed over a sand-bath for three hours. The clear solution on standing deposited crystals. They were filtered and washed with dry petroleum. They were soluble in acetic acid, alcohol, benzene, acetone and chloroform, and sparingly soluble in ether and petroleum. The mass was crystallised from benzene, m. p. 157—158°. (Found; Cl=18·23; S=7·88. $C_{18}H_{18}N_2O_2SCl_2$ requires Cl=17·88; S=8·06 per cent.).

This compound also decomposed as in the two previous cases. The decomposition product was insoluble in benzene and therefore it was crystallised from glacial acetic acid, m. p. 240°. It was identified as the original amide. The compound was stable when put in a desiccator over concentrated sulphuric acid.

Chemical Laboratory,
Baroda College.

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IX.—Interaction of Sulphuryl Chloride with Substances Containing the Reactive Methylene (CH_2) Group.

By Kuverji Gosai Naik and Mohanlal Laxmidas Shah.

The reactivity of the hydrogens of a methylene (—CH_2—) group in compounds containing —$CO \cdot CH_2 \cdot CO$— and $CN \cdot CH_2 \cdot CO$— has been taken advantage of in numerous condensations. Some light has been thrown on the factors which govern the reactivity of the methylene group, in substituted malonamides, with the help of sulphur monochloride (Naik, *J. Chem. Soc.*, 1921, **119**, 379; 1921, **119**, 1231; (Naik and Avasare, ibid, 1922, **121**, 2592; Naik and Patel, *J. Indian Chem. Soc.*, 1924, **1**, 27). It was decided to carry this subject further by studying the interaction of substituted malonamides and sulphuryl chloride. The results show that sulphuryl chloride can react as a chlorinating agent on the methylene group, and, also, in certain cases, on aromatic nuclei.[1]

In view of chlorination having been already effected with the help of sulphuryl chloride, it was expected that in the substituted malonamides containing aromatic nuclei, the chlorine might attack both the methylene group and the aromatic nucleus, and that only when the reactivity of both

1 Chlorination with sulphuryl chloride seems to have been studied by various workers (*Zeit. Chem. von Beilstein u. Hubner*, 1866, **2**, 705; Dubois, *Bull. Acad. roy. Belg.*, 1876, **42**, 126; Tohl and Eberhardt, *Ber.*, 1893, **26**, 2940; Peratoner, *Gazzetta*, 1894, **24**, 1 236; Wohl. D.R.-PP. 139552, 1467/1902, 160102/1902, 162394/1903; Silberrad, *J. Chem. Soc.*, 1921, **119**, 2029; *ibid*, 1922, **121**, 1015; Durrans, *J. Chem. Soc.*, 1922, **121**, 44; Elber and Klemm, *Ber.*, 1922, **55**, 217; Macbeth, *J. Chem. Soc.*, 1922, **121**, 1116; *ibid*, 1923, **123**, 1122; Durrans, *J. Chem. Soc.*, 1923, **123**, 1424; Bulow and King. *Annalen*, 1924, **439**, 211; Fuchs and Katschor, *Ber.*, 1924, **57** [B], 1256; Silberrad and Parke, *J. Chem. Soc.*, 1925, **127**, 1724; Silberrad, *J. Chem. Soc.*, 1925, **127**, 2677.)

the hydrogens of the methylene group $—CH_2—$, was sufficiently modified by the proximity of other groups, that sulphuryl chloride would attack the nucleus. This has been found to happen in certain cases.

The main results of the interaction of sulphuryl chloride with various mono- and di-substituted amides of malonic and methylmalonic acids can be summarised as under :—

I. *Conversion of the group* $—CH_2—$ *into* CCl_2,

(*a*) without chlorination of the nucleus: malondiphenylamide, malondibenzylamide, malondi-*o*-tolyamide, malondi-*p*-tolylamide; malon-dipropylamide and malon-mono-*p*-tolylamide undergo this change;
(*b*) with chlorination of the nucleus; malon-di-*m*-tolylamide, malon-mono-phenylamide and malon-di-β-naphthylamide undergo this change.

II. *Conversion of the group* $—CH_2—$ *into* $-CHCl—$

(*a*) without chlorination of the nucleus: malon-dimethylphenylamide undergoes this change;
(*b*) with chlorination of the nucleus: malon-di-α-naphthylamide undergoes this change.

III. *Conversion of the group* $—CH(CH_3)—$*into* $CCl(CH_2Cl)$: methylmalondiphenylamide, methylmalon-di-*o*-tolylamide and methylmalon-di-*p*-tolylamide undergo this change.

Type I. (*a*). Malondiphenylamide reacts with sulphuryl chloride as under :—

$$(PhNH{\cdot}CO)_2CH_2 + 2Cl_2SO_2 = \underset{(I)}{(PhNH{\cdot}CO)_2CCl_2} + 2HCl + 2SO_2$$

That the substance produced from malon diphenylamide has the constitution follows from the facts enumerated below :—

(1) The two hydrogen atoms that are replaced by chlorine, are not supplied by the phenyl group because (*a*) a

similar dichloroderivative is obtained from malondipropylamide; (*b*) the chlorine atoms can be replaced again by hydrogen with production of the original amide by the action of sodium hydrosulphide (Brand, *Ber.*, 1906, **42**, 3464), and by potassium iodide and hydrochloric acid (Meyer, *Annalen*, 1911, **380**, 212).

(2) The hydrogen atoms that are replaced by chlorine are not attached to the nitrogen atoms, because malon-dimethylanilide, where there is no hydrogen attached to the nitrogen, yields a monochloro-derivative.

Type I (*b*). In the case of malon-*m*-tolylamide, the reaction was more vigorous (giving rise to a tetrachloro-derivative) than with the corresponding *o*- and *p*-compounds.

$$(C_7H_7{\cdot}NH{\cdot}CO)_2CH_2+4SO_2Cl_2=(C_7H_6Cl{\cdot}NH{\cdot}CO)_2CCl_2 \\ +4HCl+4SO_2$$

Of the four chlorine atoms present in this compound, two are attached to the methylene carbon as is evident by the reduction with potassium iodide and concentrated hydrochloric acid. The other two halogen atoms which are present in the compound, even after reduction, may be present either in the ortho- or para-position to the amino-group in the aromatic-nucleus.

On studying the behaviour of malon-di-β-naphthylamide with sulphuryl chloride, there was a copious evolution of hydrogen chloride and sulphur dioxide. The tetrachloro-compound thus formed lost, on reduction by the above method, two atoms of chlorine, which were attached to the methylene carbon. Malon-monophenylamide exhibits a similar reactivity, and the reaction proceeds as under :—

$$\begin{matrix} NH_2{\cdot}CO \\ C_6H_5{\cdot}NH{\cdot}CO \end{matrix}\!>\!CH_2+3SO_2Cl_2=\begin{matrix} NH{\cdot}CO \\ C_6H_4Cl{\cdot}NH{\cdot}CO \end{matrix}\!>\!CCl_2+SO_2+3HCl$$

Type II (*a*). The interaction of malon-dimethylphenylamide with sulphuryl chloride results in the production of a monochloro compound.

$$[CH_3(C_6H_5)N\cdot CO]_2CH_2 + SO_2Cl_2 = [CH_3(C_6H_5)N\cdot CO]_2CHCl + HCl + SO_2$$

In spite of the two hydrogen atoms of the methylene group being available only one is attacked. This course of the reaction is not an abnormal one, as is evident from the work of Naik (*loc. cit.*) and West (*J. Chem. Soc.*, 1922, **121**, 2196).

Type II (*b*). When α-naphthylamide was made to react with sulphuryl chloride in the ratio of 1 : 3, a trichloro-compound was obtained.

$$C_{10}H_7\cdot NH\cdot CO)_2CH_2 + 3Cl_2SO_2 = (C_{10}H_6Cl\cdot CO)_2CHCl + 3HCl + 3SO_2.$$

That in this trichloro-compound, only one chlorine is attached to the methylene carbon, and the other two are substituted in the aromatic nuclei, is shown by the study of its reduction with potassium iodide and hydrochloric acid.

It is curious that maton-di-α-naphthylamide gives a trichloroderivative, whereas the corresponding β-compound gives a tetrachloro-derivative under similar conditions. That the difference between the behaviour of α-naphthyl compounds and β-naphthyl compounds is general was noticed by other workers (Whiteley, J. *Chem. Soc.*, 1903, **83**, 24), and was attributed to various reasons (Weinberg, *Ber.*, 1924, **54**[**B**], 2168).

Type III. Further, it was desirable to see if the same type and reactivity persisted amongst the corresponding derivatives of methylmalonic acid. Here one of the hydrogen atoms of the methylene group is replaced by the methyl group, so that a monochloro derivative might be expected on interaction with sulphuryl chloride. Yet, in the three cases that were studied, dichloro-derivatives were formed. On reduction of these by the usual method it was found that both the chlorine atoms were replaced by hydrogen. Hence the second chlorine atom must have entered the methyl

radicle. If the second chlorine atom had entered the benzene nucleus, it could not have been reduced by the above method, nor could it have come in place of the hydrogen of the imino (—NHR—) group, as was pointed out previously. Thus :

$$(R{\cdot}NH{\cdot}CO)_2CH{\cdot}CH_2 + 2SO_2Cl_2 = (R{\cdot}NH{\cdot}CO)_2CCl{\cdot}CH_2Cl + 2HCl + 2SO_2$$

where R represents either a phenyl or a tolyl group).

The above dichloro-compounds showed no trace of any free hydrogen chloride contained in them; for, when they were shaken with water, the filtrate gave no reaction with silver nitrate. Examples of chlorination similar to this are known (*cf.* Willgerodt and Durr, *Ber.*, 1887, **20**, 539). The mechanism of this interesting course of chlorination is discussed later on.

Coming to the question of reactivity of the hydrogens of the methylene group in grouping such as $—CO{\cdot}CH_2{\cdot}CO—$, $CN{\cdot}CH_2{\cdot}CO—$ etc., it is interesting to note that the experiments described here afford clear evidence that the interaction of sulphuryl chloride with compounds containing the methylene radicle depends on the total negativity of the groups attached to the two remaining valencies of the carbon atom (*loc. cit.*) If these valencies carry neutral groups such as $\cdot CO{\cdot}NH_2$, as in malonamide no interaction occurs with sulphuryl chloride. If, however, the neutral character of either or both of the carboxylamide groups is disturbed by the entrance of phenyl, tolyl, etc., interaction with sulphuryl chloride readily occurs.

The reactivity of sulphuryl chloride with malonic ester, acetoacetic ester, cyanacetic ester etc., has been studied by Macbeth J. *Chem. Soc.*, 1922, **121**, 1120; 1923, **123**, 1125), who obtained chloro-compounds. In all such

cases, the reactivity of the sulphuryl chloride with esters was found to be great, certainly greater than the reactivity of the corresponding amido and substituted amido derivatives.

Although no definite measurements have as yet been made, it is evident that the speed of the reaction depends on the total negativity of the attached groups. For example, sulphuryl chloride reacts more vigorously with compound (*iii*, R=Ph) than with (*ii*, R=Tol) whilst the reaction with the ester itself is the most vigorous, even taking place at the ordinary temperature. So in a series like.

(*i*) $CH_2\cdot(CONH_2)_2$
(*ii*) $NH_2\cdot CO\cdot CH_2\cdot CO\cdot NHR$ (R=Ph, Tol etc.)
(*iii*) $CH_2\cdot(CONHR)_2$
(*iv*) $CH_2\cdot(COOC_2H_5)_2$

the reactivity which is absent in (*i*) is found in (*ii*) and goes on increasing through the series (Naik, *loc. cit.*).

The reactivity of the CH_2 group may be referred to (*a*) polarity (Macbeth and his collaborators, *J. Chem. Soc.*, 1922, **121**, 892, 904, 1109, 1116, 2169, 2527, 2601; 1923, **123**, 124, 1122; 1925, **127**, 892, 1118), (*b*) to keto-enol transformation (Thorpe and his collaborators. *J. Chem. Soc.*, 1911, **99**, 2183; 1921, **119**, 1203; 1922, **121**, 1896), or (*c*) to the combined influences of polarity effects, steric influence and structural characteristics such as would give rise to keto-enol transformations (West, *J. Chem. Soc.*, 1924, **125**, 710).

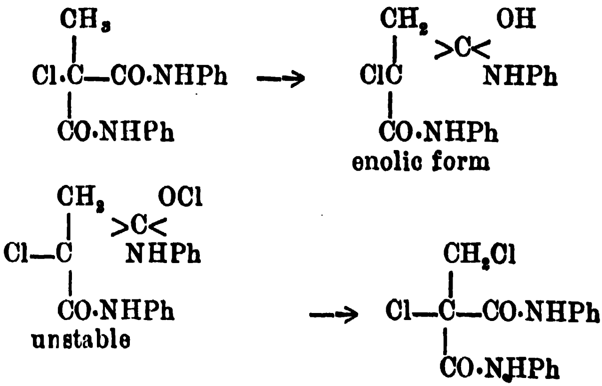
The reactivity of the compounds investigated herein can be explained on the basis of keto-enol transformation. In the cases where both the hydrogens of the methylene group are replaced by chlorine stoms, the substance, according to Norris and Thorpe (*J. Chem. Soc.*, 1921, **119**, 1203), assumes an enolic form. Thus in the case of formation of compound I, the course followed can be represented thus:

$$PhNH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHPh \longrightarrow PhNH{\cdot}CO{\cdot}CH{:}\ C(OH){\cdot}NHPh$$
$$\xrightarrow{Cl_2} PhNH{\cdot}CO{\cdot}CH{:}C(OCl){\cdot}NHPh \quad \text{unstable}$$
$$\longrightarrow PhNH{\cdot}CO{\cdot}CHCl{\cdot}CO{\cdot}NHPh.$$

By a similar series of changes the final product is the dichloro-compound, $CCl_2(CONHPh)_2$.

In the case of malon-dimethylphenylamide, only one hydrogen is reactive. It appears that after one of the two hydrogen atoms has reacted, the other becomes sluggish, only a monochloro-compound being obtained. West (*loc. cit.*) has shown that further chlorination of this amide is not possible on passing more chlorine. This sluggishness of the second hydrogen atom can be explained as being due to the stability of the keto-form as in the case of acetyl acetone (Norris and Thorpe, *loc. cit.*), which gives a monobromo-compound, $(CH_3{\cdot}CO)_2CHBr$. Further bromination does not take place.

In some cases, however, enolisation involves a hydrogen atom of a terminal methyl group. For example, in the case of methylmalondiphenyl amide, after the group $—C(CH_3)Cl$ has been formed, enolisation involves a hydrogen atom of the methyl group:



Such a change due to the enolisation of a terminal methyl group was noticed by Hantzsch (*Ber.*, 1894, **27**, 356, 3168).

EXPERIMENTAL.

Dichloromalondiphenylamide.

Malondiphenylamide (2 g.) was made to react with sulphuryl chloride (2·25 g.) in presence of dry benzene (50 c.c.). The mixture was refluxed for four hours over a water-bath. Dense fumes of sulphur dioxide and hydrogen chloride were evolved. When the reaction was over, the solution was filtered hot and the filtrate, on cooling, deposited a white crystalline mass. This was filtered, washed repeatedly with dry petroleum to free it from excess of sulphuryl chloride, and crystallised from hot benzene, m.p. 127°.

It is fairly soluble in acetone, chloroform, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid and carbon tetrachloride, and insoluble in light petroleum. (Found: Cl, 21·8, $C_{15}H_{12}N_2O_2Cl_2$ requires Cl, 21·96 per cent.).

Reduction of the above Compound with Hydriodic Acid.—The dichloro-compound (0·1498 g.) was dissolved in absolute alcohol (30 c.c.). To the solution, potassium iodide (1·85 g.) dissolved in water (20 c.c.) was added, and then concentrated hydrochloric acid (10 c.c.). The mixture was refluxed for 3 hours at about 60°. A control experiment was set up at the same time with the same amount of absolute alcohol, potassium iodide and concentrated hydrochloric acid, for the same period; and from the observations in the control experiment, a correction was introduced in the observations of the actual reduction experiment. The substance liberated iodine equivalent to 19·3 c.c. of 0·0971*N* sodium thiosulphate solution. (Found: Cl (equivalent of the iodine liberated), 22·16. $C_{15}H_{12}N_2O_2Cl_2$ requires Cl, 21·96 per cent.).

Reduction of Dichloromalondiphenylamide with alkaline Hydrosulphide.—The chloride (2 g.) was added to absolute alcohol (20 c. c.) and refluxed for about half an hour. An aqueous solution of sodium hydrosulphide, prepared by

saturating sodium hydroxide (0·3 g.) dissolved in a small quantity of water with hydrogen sulphide, was gradually added to it. After a time the whole went into solution with a brown colour. On cooling a slight crystalline precipitate appeared. The solution was diluted with water (500 c.c.) and filtered. The substance was washed free from alkali by hot water. The product was then crystallised from acetic acid, and was found to be pure melondiphenylamide, m.p. 224-225°.

Dichloromalon-dibenzylamide.

This substance was prepared from malon-dibenzylamide (2 g.), and sulphuryl chloride (2 g.) in presence of dry benzene (50 c c) as before. It was deposited as a white mass sparingly soluble in benzene, from which it was crystallised in white shining plates, m.p. 170-171°.

It is fairly soluble in chloroform, sparingly so in benzene, alcohol, acetone, toluene, acetic acid, carbon tetrachloride, ethyl acetate, carbon bisulphide, ether and nitrobenzene, but insoluble in light petroleum. (Found: Cl, 19·82. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20·20 per cent.

*Dichloromalon-di-*o*-tolylamide.*

This substance was prepared from malon-di-*o*-tolylamide (2 g.) and sulphuryl chloride (2 g.) in the usual way. The white solid is sparingly soluble in alcohol, from which it was crystallised in white needles, m. p. 140-141°.

It is fairly soluble in acetone, chloroform, ethyl acetate, carbon bisulphide and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid, carbon tetrachloride and ether, but insoluble in light petroleum. (Found : Cl, 20·15. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20·20 per cent.).

*Dichloromalon-di-*p*-tolylamide.*

The above compound was obtained as a white amorphous powder when malon-di-*p*-tolylamide (2 g.) was treated with sulphuryl chloride (2 g.) in the usual way. It was crystallised from alcohol in shining white needles, m. p. 145-146°.

It is fairly soluble in benzene, acetone, chloroform, toluene, acetic acid, ethyl acetate, carbon bisulphide, ether and nitrobenzene, sparingly so in alcohol and carbon tetrachloride, but insoluble in light petroleum. (Found : Cl, 20.01. $C_{17}H_{16}O_2N_2Cl_2$ requires Cl, 20.20 per cent.).

Dichloromalon-dipropylamide.

It was prepared by the action of sulphuryl chloride (3 g.) on malon-dipropylamide (2 g.) in the usual way. The solid product was crystallised from benzene in shining cubes, m. p. 108-109°.

It is fairly soluble in acetone, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, ethyl acetate, carbon bisulphide, ether and nitrobenzene, but insoluble in light petroleum. (Found : Cl, 27.83. $C_9H_{16}O_2N_2Cl_2$ requires Cl, 27.82 per cent.)

*Dichloromalon-mono-*p*-tolylamide.*

It was prepared from malon-mono-*p*-tolylamide (2 g) and sulphuryl chloride (2 g.) in the usual way. A white solid was obtained, which on crystallisation from benzene melted at 145-146°.

It is fairly soluble in acetone, ethyl acetate and ether, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon bisulphide and nitrobenzene, but almost insoluble in petroleum and carbon tetrachloride. (Found : Cl. 27.1. $C_{10}H_{10}O_2N_2Cl_2$ requires Cl, 27.17 per cent.).

*Preparation of Malon-di-*m*-tolylamide.*

Malonic ester and pure *m*-toluidine were taken in molecular proportions in a flask provided with a cork, through which a wide tube passed. This tube was bent at the top and was fitted into a condenser. The length of the tube from the cork upwards to the bend at the top measured 15 cm. The flask was put in a paraffin-bath and maintained at 130-110° for four hours, when alcohol distilled off drop

by drop. The temperature at the end was raised to 150°. The rate of the distillation was so regulated that for every drop of alcohol distilled, fifteen drops of the liquid returned to the flask. This increased the yield of the diamide. The liquid was then transferred to a mortar, where it solidified on cooling. The solid was extracted with alcohol and finally washed with a little ether. When crystallised from acetic acid, it was obtained in brilliant needles, m. p. 152°.

It is fairly soluble in chloroform, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, acetone, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and ether, but almost insoluble in light petroleum. (Found : N, 9.8. $C_{17}H_{18}O_2N_2$ requires N, 9.9 per cent.).

Dichloromalon-di-m-tolylamide dichloride.

On treating malon-di-*m*-tolylamide (2 g.) with sulphuryl chloride (4 g.) in the usual way a white mass was deposited on standing. The resulting product was crystallised from benzene in cubic crystals, m. p. 164°.

It is fairly soluble in acetone, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, ethyl acetate, ether and nitrobenzene, but almost insoluble in carbon tetrachloride and light petroleum. (Found: Cl, 33.51. $C_{17}H_{14}O_2N_2Cl_4$ requires Cl, 33.78 per cent.).

Dichloromalon-monochlorphenylamide.

This compound was prepared from malon-mono-phenylamide (2 g.) and sulphuryl chloride (3 g.) in the same way as the preceding chloride. After the reaction was over, the product crystallised immediately on cooling. On recrystallising from benzene, it yielded shining pearly plates, m. p. 136°.

It is fairly soluble in acetone, ethyl acetate and ether, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and nitroben-

zene, but almost insoluble in light petroleum. (Found: Cl, 37·67. $C_9H_7O_2N_2Cl_3$ requires Cl, 37·80 per cent.).

Dichloromalon-di-β-naphthylamide dichloride.

The above compound was obtained as a white amorphous powder, when malon-di-β-naphthylamide and sulphuryl chloride were treated in the usual way. It was crystallised from benzene, in which it is difficultly soluble, in shining crystals, m. p. 183°.

It is sparingly soluble in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, ethyl acetate and nitrobenzene, but almost insoluble in light petroleum, acetone, carbon bisulphide and ether. (Found: Cl, 29·25. $C_{23}H_{14}O_2N_2Cl_4$ requires Cl, 28·84 per cent.).

Monochloromalon-dimethylphenylamide.

Malondimethyl-phenylamide (2 g.) and sulphuryl chloride (2 g.) were made to react in the usual way described. The amorphous white product, when crystallised from absolute alcohol, yielded colourless prisms, m. p. 187°.

It is fairly soluble in chloroform, sparingly so in acetic acid, ethyl alcohol, acetone, toluene, ethyl acetate, nitrobenzene, and carbon bisulphide, but nearly insoluble in light petroleum, carbon tetrachloride and ether. (Found: Cl, 11·44. $C_{17}H_{17}O_2N_2Cl$ requires Cl, 11·2 per cent.).

This chloro-compound was prepared by West (J. *Chem. Soc.*, 1922, **121**, 2196) by direct chlorination of the amide.

Chloromalon-di-α-naphthylamide dichloride.

This compound was prepared from malon-di-α-naphthylamide (2 g.) and sulphuryl chloride (2·5 g.) in the usual way. The mass obtained, when crystallised from benzene, gave pure shining cubic crystals, m. p. 182°.

It is fairly soluble in chloroform and nitrobenzene, sparingly so in benzene, alcohol, acetone, toluene, acetic

acid and ethyl acetate, but nearly insoluble in light petroleum, carbon tetrachloride, carbon bisulphide and ether. (Found : Cl, 23.41. $C_{23}H_{15}O_2N_2Cl_3$ requires Cl, 23.23 per cent.).

Chloromethyle-chloromalondiphnylamide.

The above substance was prepared from methylmalondiphenylamide (2 g.) and sulphuryl chloride (2 g.) in the usual way. The solid was precipitated from a large quantity of petroleum. On crystallisation from a small amount of benzene, it gave shining pearly plates, m.p. 128°.

It is fairly soluble in acetone, ethyl acetate, chloroform, ether and nitrobenzene, sparingly so in benzene, alcohol, toluene, acetic acid, carbon tetrachloride and carbon bisulphide, but almost insoluble in light petroleum. (Found: Cl, 21.18. $C_{18}H_{14}O_2N_2Cl_2$ requires Cl, 21.05 per cent.).

Chloromethyl-chloromalon di-o-tolylamide.

This compound was obtained from methylmalon-di-*o*-tolylamide (2 g.) and sulphuryl chloside (2 g.) as above. The white solid, on crystallisation from a benzene-petrol mixture, gave a feathery mass, m. p. 130°.

It is fairly soluble in acetone, ethyl acetate and nitrobenzene, sparingly so in benzene, alcohol, chloroform, toluene, acetic acid, carbon tetrachloride, carbon bisulphide and ether, but insoluble in light petroleum, (Found; Cl, 19.83. $C_{18}H_{18}O_2N_2Cl_2$ requires Cl, 19.43 per cent.).

*Chloromethyl-chloromalon-di-*p*-tolylamide*

The above compound was obtained as shining white needles, when methylmalon-di-*p*-tolylamide (2 g.) and sulphuryl chloride (2 g.) were made to react in the usual way. It was recrystallised from benzene, in which it is sparingly soluble: m.p. 138°.

The solubility of the chloride was of the same order as the preceding chloride. (Found: Cl, 1981. $C_{18}H_{18}O_2N_2Cl_2$ requires Cl. 19.43 per cent.).

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Chemistry Department,
The College, Baroda.

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X—Interaction of Sulphur Monochloride with Organic Compounds containing the reactive Methylene (—CH_2—) Group. Formation and Properties of Dithioketones ($R_2C:S:S$) and Dithioethers ($R_2S:S$). Part IV

BY KUVERJI GOSAI NAIK AND YESHWANT NARAYAN BHAT.

The work described in this communuication is a continuation of the work already published by one of the authors (Naik, J. *Chem. Soc.*, 1921, **119**, 379, 1231; 1922, **121**, 2592.) It was then suggested that sulphur monochloride appears to react in two forms:

$$(i)\ S{=}S\begin{array}{l}\diagup Cl\\ \diagdown Cl\end{array} \quad \text{and} \quad (ii)\ \begin{array}{l}S{-}Cl\\ \vert\\ S{-}Cl\end{array}$$

Whereas the formation of stable dithio-compounds points to the fact that S_2Cl_2 appears to react in form (*ii*), it would be indeed difficult to explain the formation of mustard gas on any other assumption than that sulphur monochloride reacts in form (*i*) (*loc. cit.*) :

$$2\ CH_2 : CH_2 + Cl_2\ S:S \begin{array}{l}\nearrow (CH_2Cl.CH_2)_2S:S\\ \searrow (CH_2Cl.CH_2)_2S+S\end{array}$$

As reported before the dithio-grouping resulting from the interaction of sulphur monochloride with amides of malonic ester is very stable, for the resulting di-thioketones and dithio-ethers could be easily nitrated with fuming nitric acid without affecting the dithio-grouping.

The interactions of sulphur monochloride with (1) malon-di-ethylamide, (2) malon-di-*n*-propylamide, (3) malon-di-*iso*butylamide, (4) malon-di-*n*-heptylamide, (5) malon-di-*m*-

toluidide and (6) methylmalon-di-*m*-toluidide and (7) methyl malon-dibenzylamide were examined. Of these, malon-di-*n*-heptylamide, malon-di *m*-toluidide and methyl-malon-dibenzylamide were prepared for the first time. Whereas (*a*) compounds (1), (2), (3), (4) and (5) interacted to give dithioketones of the general formula

$$\begin{array}{c} R \\ \\ R \end{array}\!\!>C<\!\begin{array}{c} S \\ | \\ S \end{array}$$

(*b*) compound (6) gave the dithio-ether of the general formula, $R{\cdot}C(CH_3).S{\cdot}S{\cdot}C(CH_3)R$.

Thus,

$$\text{(a)}\quad \begin{array}{l} R{\cdot}NH{\cdot}CO \\ \\ R{\cdot}NH{\cdot}CO \end{array}\!\!>CH_2 + \begin{array}{c} Cl{-}S \\ | \\ Cl{-}S \end{array} \longrightarrow \begin{array}{l} R{\cdot}NH{\cdot}CO \\ \\ R{\cdot}NH{\cdot}CO \end{array}\!\!>C<\!\begin{array}{c} S \\ | \\ S \end{array}$$

and

$$\text{(b)}\quad \begin{array}{c} (R{\cdot}NH{\cdot}CO)_2CHMe \\ + \\ (R{\cdot}NH{\cdot}CO)_2CHMe \end{array} \begin{array}{c} Cl{-}S \\ | \\ Cl{-}S \end{array} \longrightarrow \begin{array}{r} (R{\cdot}NH{\cdot}CO)_2{-}C(Me)S \\ | \\ (R{\cdot}NH{\cdot}CO)_2{-}C(Me)S \end{array}$$

where R may be an ethyl, propyl, *iso*butyl, heptyl or tolyl group.

On nitration with fuming nitric acid, the dithio-compound derived from (5) gave a tetranitro-derivative, thus:

$$\begin{array}{c} S \\ | \\ S \end{array}\!>C<\!\begin{array}{l} CO{\cdot}NH{\cdot}C_7H_7 \\ \\ CO{\cdot}NH{\cdot}C_7H_7 \end{array} \xrightarrow[HNO_3]{\text{fuming}} \begin{array}{c} S \\ | \\ S \end{array}\!>C<\!\begin{array}{l} CO{\cdot}NH{\cdot}C_7H_5(NO_2)_2 \\ \\ CO{\cdot}NH{\cdot}C_7H_5(NO_2)_2 \end{array}$$

From this, it may be suggested that the dithio-grouping in compounds of the above type, may be structurally different from that present in $\beta\beta'$ dichlor-diethyldisulphide and such allied compounds. It also lends further support to the suggestion previously made, that sulphur monochloride may react in two forms (*i*) and (*ii*) and when it reacts in form (*i*), it gives rise to very stable dithio-compounds having the groupings

$$\begin{array}{c} S \\ | \\ S \end{array}\!>C< \quad \text{and} \quad \begin{array}{l} S{-}C{-} \\ | \\ S{-}C{-} \end{array}$$

Experimental

Interaction of Malon-diethylamide with Sulphur Monochloride.—Malon diethylamide was prepared by Whiteley's method (J. *Chem.* Soc., 1921, **119**, 366) by the condensation

of ethylmalonate (16 g.) with ethylamine (30 g. of 33 per cent solution). It was crystallised from benzene, m.p. 149°.

Malondiethylamide (2 g.) was put in a flask with 30 c.c. of dry benzene. Sulphur monochloride (2 g.) was added to it, and the flask was refluxed on a sand-bath for three hours. Hydrogen chloride began to evolve moderately on heating. Within 15 minutes, a solid separated, and bumping began which had to be controlled. The solid was separated by filtering the solution at the pump, and was washed with dry petroleum to remove the adhering sulphur monochloride.

It is very soluble in acetone, ethylacetate, acetic acid and chloroform; less so in methyl alcohol, ethyl alcohol, benzene and toluene; sparingly soluble in carbon tetrachloride, carbon bisulphide and ether, and insoluble in petroleum. It was crystallised from absolute alcohol. It shrinks at 186° and melts at 202°. (Found: N, 12.97; S, 29.46. $C_7H_{12}N_2O_2S_2$ requires N, 12.73; S, 29.09 per cent.).

*Malon-di-*n*-propylamide and* Sulphur *Monochloride.*—Malon-di-*n*-propylamide was prepared by Whiteley's method (*loc. cit.*). Ethylmalonate (9.5 g.) and *n*-propylamine were taken in a sealed tube and, after 24 hours, were heated at 125°—130° for six hours. The mixture solidified when allowed to remain at the ordinary temperature for some hours. The sealed tube was then opened, and the white solid was washed with petroleum. The m. p. of the substance, purified from benzene was 139°.

The above amide (5 g.) was condensed with sulphur monochloride (5 g.) in a similar way.

The product is very soluble in chloroform, benzene, ethyl acetate, acetone, acetic acid and nitrobenzene; less so in ethyl alcohol, methyl alcohol and toluene; sparingly soluble in carbon bisulphide and ether; and insoluble in water and petroleum. It was crystallised from absolute alcohol. It shrinks at 172° and melts at 180°. (Found: N, 10.92; S, 25.69. $C_9H_{16}O_2N_2S_2$ requires N, 11.29; S, 25.80 per cent.).

*Malon-di-*iso*butylamide and* Sulphur *Monochloride.*-Malon-di-*iso*butylamide was prepared in the same way as malon-di-*n*-propylamide, by condensing ethylmalonate (8 g.) with *iso*butylamine (7·3 g.). The product was crystallised from benzene and melted at 126°.

The above amide (2 g.) and sulphur monochloride (1·5 g.) were condensed as in the previous cases.

The white product so obtained dissolves readily in chloroform, acetic acid, ethylacetate, or nitrobenzene; less readily in benzene, toluene, methyl alcohol, ethyl alcohol and acetone; sparingly so in ether, carbon bisulphide, or carbon tetrachloride, and is insoluble in hot water or light petroleum. It was crystallised from absolute alcohol. It shrinks at 196° and melts at 202°. (Found: N, 10·43; S, 22·98. $C_{11}H_{20}O_2N_2S_2$ requires N, 10·14; S, 23·19 per cent.).

*Preparation of Malon-di-*n*-heptylamide.*—A mixture of *n*-heptylamine (11·5 g.) and ethylmalonate (8 g.) was allowed to remain in a sealed tube at the ordinary temperature for 24 hours, when it was found in a semi-solid condition. The sealed tube was then heated in a paraffin bath at 125-130° for about 7 hours. The tube was opened when cool, and the white solid was taken out and washed with petroleum. The solid thus obtained was practically pure, and weighed 12 g.

It dissolves very readily in chloroform, benzene, toluene, ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, acetone, and nitrobenzene; less readily in carbon tetrachloride and ether; and is sparingly soluble in petroleum, and insoluble in water. It crystallises from benzene and melts at 132°. (Found : N, 9·52. $C_{17}H_{34}O_2N_2$ requires N,9·40 per cent.).

*Malon-di-*n*-heptylamide and* Sulphur *Monochloride.*-Malon-di-*n*-heptylamide (3 g.) was condensed with sulphur monochloride (1·5 g.) in the usual manner. The resulting substance, being very soluble in benzene, was precipitated by petroleum. It came out as a gelatinous white mass which was filtered and washed with dry petroleum.

It is very soluble in benzene, chloroform, acetic acid, methyl alcohol, ethyl alcohol, acetone, ethyl acetate and nitrobenzene; less soluble in toluene and carbon bisulphide; and sparingly soluble in ether, petroleum, and carbon tetrachloride. It was purified from alcohol, m. p. 125°. (Found: N. 7·83; S, 17·37. $C_{17}H_{32}O_2N_2S_2$ requires N, 7·77; S, 17·77 per cent.).

*Malon-di-*m*-toluidide and Sulphur Monochloride.*—The amide (2 g.) and sulphur monochloride (1 g.) were condensed as in the previous cases.

The product is readily soluble in chloroform. acetic acid, ethyl acetate, acetone and nitrobenzene; less readily in benzene, toluene, methyl alcohol, ethyl alcohol, carbon tetrachloride and carbon bisulphide; sparingly soluble in ether and hot water, and insoluble in light petroleum. It was crystallised from absolute alcohol. It shrinks at 158° and melts at 180° to a yellow liquid. (Found : S. 18·13. $C_{17}H_{16}O_2N_2S_2$ requires S, 18·60 per cent.).

Nitration.—One gram of the above substance was added in a conical flask to 10 c. c. of fuming nitric acid (*d* 1·5). The flask was heated on a sand-bath until the evolution of oxides of nitrogen slackened. The flask was allowed to cool, when a little yellow solid came down. As the solid was too little to be filtered through the asbestos, the solution was added to some distilled water in a beaker. The precipitated solid was filtered at the pump, washed with distilled water, and allowed to dry at the ordinary temperature and powdered. The powder was dried in an air oven at 60-70°. It melts with decomposition at 166°. (Found: N, 16·32; S, 12·27. $C_{17}H_{12}O_{10}N_6S_2$ requires N, 16·03; S, 12·21 per cent.).

*Methyl malon-di-*m*-toluidide.*—Methylmalonic ester (10 g.) was condensed with *m*-toluidine (13 g.) in the same way as in the case of the corresponding malon-derivative. The temperature, in this case, was raised to 280°. The yield was very poor.

It is very soluble in benzene, toluene, chloroform, acetic acid, ethyl acetate, methyl alcohol, ethyl alcohol, acetone and nitrobenzene; less readily in carbon tetrachloride, and insoluble in petroleum. It was crystallised from benzene, m. p. 157°. (Found : N, 9·86. $C_{18}H_{20}O_2N_2$ requires N, 9·46 per cent.).

*Methyl malon-di-*m*-toluidide and* Sulphur *Monochloride.*—The above amide (2 g.) and sulphur monochloride (0·5 g.) were condensed together in the usual manner. The reaction in this case was slower than in the case of the corresponding malon-di-*m*-toluidide derivative.

The white product is readily soluble in ethylacetate, acetic acid, acetone and nitrobenzene; less readily soluble in benzene, toluene, chloroform, carbon tetrachloride, methyl alcohol and ethyl alcohol; slightly soluble in carbon bisulphide, ether and hot water and insoluble in petroleum. It was crystallised from absolute alcohol, m. p. 187°-188°. (Found: S, 9·39. $C_{36}H_{38}O_4N_4S_2$ requires S, 9·78 per cent.).

Methylmalon-di-benzylamide.—Ethylmethylmalonate (9 g.) and benzylamine (11 g.) were taken in a round bottomed flask and heated at 150-160° as in the case of other amides. The white product so obtained readily dissolves in benzene, toluene, chloroform, methyl alcohol, ethyl alcohol, acetone, ethylacetate, acetic acid and nitrobenzene; less readily in chloroform, and is sparingly soluble in carbon bisulphide, ether, petroleum and hot water. It was purified from benzene, m. p. 142°. (Found: N, 9·66. $C_{18}H_{20}O_2N_2$ requires N, 9·46 per cent.).

We take this opportunity to record our thanks to the Government of His Highness The Maharaja Gaekwar of Baroda for a grant which has defrayed the expense of this investigation.

Chemistry Department,
The College Baroda.

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XI—Condensation of Cyanacetic Ester with some Aryl and Alkylamines. Preparation of some Aryl and Alkyl substituted Cyanacetamides.

By KUVERJI GOSAI NAIK AND YESHWANT NARAYAN BHAT.

The method adopted in the preparation of these compounds was a modification of that employed by Freund (*Ber.*, 1884, **17**, 134) and Whiteley (*J. Chem. Soc.*, 1903, **83**, 24), in the preparation of malondiphenylamide.

Cyanacetanilide [*Compt. rend.*, 1895, **121**, 189; Queuda, *Chem. Centrr.*, 1892, i, 283 from *Atti. R. Accad. Sci. Torino*, 27; Warapsky and Hillers, J. *pr. Chim.*, (ii), **92**, 297], cyanacet-*p*-toluidide (Grothe, *Arch. Pharm.*, **238**, 608; Haller, *Compt. rend.*, 1889, **108**, 1116), cyanacetbenzylamide (Guareschi, *Chem. Centr.*, 1892, i, 382 from *Atti R. Accad. Sci. Torino*, 27) and cyanacetxylidide m.p. 167°) are already known.

(1) Cyanacet-*o*-toluidide, (2) cyanacet-*m*-toluidide (3) cyanacet-α-naphthylamide, (4) cyanacet-β-naphthylamide,(5) cyanacet-*adj.*-*m*-xylidide, (6) cyanacetmethyl-amide and (7) cyanacetethylamide were prepared for the first time. The methods employed had to be varied with the varying basic nature of the amines, more drastic method being employed in the case of those amines which possessed feeble ammoniacal characteristics.

Benzylamine resembles, though remotely, the paraffin amines and hence the method of preparing an amide, with the help of this amine has to be modified from that adopted in the previous cases. Aniline, toluidines and naphthylamines possess ammoniacal characteristics to a very feeble extent indeed, and in their cases, more drastic methods for the production of the substituted derivatives were employed. We can thus roughly divide the preparations of the amides into three division :—

A. Cyanacetmethylamide; cyanacetethylamide.

B. Cyanacetbenzylamide.

C. Cyanacetanilide; cyancet-*p*-toluidide; cyanacet-*o*-toluidide; cyanacet-*m*-toluidide; cyanacet-α-naphthylamide; cyanacet-β-naphthylamide; cyanacet-*adj*.-*m*-xylidide.

Of the above substituted amides, cyanacetanilide, cyanacet-*p*-toluidide and cyanacetbenzylamide are known, but no reliable details of the methods employed in their preparations could be found. The melting points of these substances fairly agree with those reported and the analyses confirm the percentage of nitrogen required.

Experimental.

Preparation of Substituted Amides of Cyanacetic Ester.

In the preparation of substituted amides of the aromatic series Whiteley's method (J. *Chem. Soc.*, 1903, **83**, 24) with the modification described by Naik (J. *Chem. Soc.*, 1921, **119**, 379) was followed.

Cyanacetanilide.—Ethyl cyanacetate (37 g.) and pure redistilled aniline (45 g.) were mixed together in a round-bottomed flask provided with a wide upright bent tube, one end of which passed through a cork in the mouth of the flask and the other end was attached to the condenser. The flask was kept at 160°—170° for six hours. The height of the upright portion of the bent tube was so adjusted that for every drop of alcohol distilled over, a dozen drops of the liquid went back to the flask. This was to avoid any of the reacting liquids coming over unchanged. The temperature was slowly raised to 180° till no more alcohol came over. The contents of the flask, when hot, were then poured into a porcelain mortar where the whole solidified. The colour of the liquid when taken out of the bath was red. The solid cake was broken and triturated with a mixture of equal volumes of benzene and light petroleum, and filtered at the pump. The process was repeated until the reddish colour of the solid disappeared. The yield was 66 per cent.

Cyanacetanilide is readily soluble in methyl alcohol, ethyl alcohol, acetone, acetic acid, ethyl acetate and nitrobenzene; and insoluble in light petroleum (b. p. 50-60°), carbon tetrachloride, carbon disulphide and xylol. It was crystallised from alcohol as white needles, m. p. 198-199°. (Found: N, 17·63. $C_9H_8N_2O$ requires N, 17·50 per cent.).

Cyanacet-p-*toluidide*.—Cyanacet-*p*-toluidide was prepared from ethyl cyanacetate (20 g.) and freshly distilled *p*-toluidine (21 g.) in the same way as cyanacetanilide.

The white product so obtained is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, ethyl acetate, acetone and nitrobenzene, less so in benzene, toluene and chloroform; sparingly soluble in carbon tetrachloride and hot water, and insoluble in ether, light petroleum and carbon bisulphide. It was crystallised from alcohol, m. p. 180°. (Found: N, 15·71. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-o-*toluidide*.—Ethyl cyanacetate (34 g.) and *o*-toluidine (29 g.) were condensed together in a similar way.

The white product is readily soluble in benzene, methyl alcohol, ethyl alcohol, ethyl acetate, acetic acid, chloroform, acetone and nitrobenzene; less readily so in carbon tetrachloride, very sparingly soluble in hot water and petroleum, and insoluble in carbon bisulphide and ether. It was crystallised from alcohol as thin plates, m. p. 125° (Found: N, 15·90. $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-m-*toluidide*.—Ethyl cyanacetate (15 g.) and *m*-toluidine (13 g.) were condensed in the usual manner. The solid was triturated and washed with ether.

It is readily soluble in methyl alcohol, ethyl alcohol, acetic acid, ethyl acetate, acetone and nitrobenzene; less readily in benzene, toluene, chloroform and hot water; sparingly soluble in carbon tertrachloride, carbon bisulphide and ether; and insoluble in petroleum. It separated from benzene in the form of white needles, m. p. 132°. (Found; N, 16·25, $C_{10}H_{10}N_2O$ requires N, 16·09 per cent.).

Cyanacet-α-naphthylamide.—Ethyl cyanacetate (22 g.) and α-naphthylamine (25 g.) were similarly condensed. The product was finally washed with alcohol until the reddish colour of the solid was removed.

It is freely soluble in ethylacetate, acetic acid, acetone, and nitrobenzene; less soluble in methyl alcohol, ethyl alcohol, benzene, toluene and chloroform; sparingly soluble in carbon tetrachloride, carbon bisulphide, petroleum, ether and hot water. It was crystallised from acetic acid, m. p. 175°. (Found: N, 13.65. $C_{13}H_{10}N_2O$ requires N, 13.33 per cent.).

Cyanacet-β-naphthylamide.—Ethyl cyanacetate (25 g.) and β-naphthylamine (22 g.) were condensed as in the previous cases.

The white solid so obtained is very soluble in ethyl acetate, acetic acid, acetone and nitro-benzene; less so, in benzene, toluene, chloroform, hot water and methyl alcohol, ethyl alcohol; sparingly soluble in carbon tetrachloride, carbon bisulphide and ether; and insoluble in light petroleum. It was crystallised from alcohol, m. p. 174°. (Found: N, 13.18. $C_{13}H_{10}N_2O$ requires N, 13.33 per cent.).

Cyanacet-adj-m-*xylidide.*—Ethyl cyanacetate (11 g.) and *adj-m*-xylidine (12 g.) were condensed in the usual manner. The product is readily soluble in ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, acetone and nitrobenzene; less so in benzene, toluene and chloroform and very slightly soluble in petroleum, hot water, carbon tetrachloride, carbon bisulphide and ether. It was crystallised from alcohol, m. p. 107°. (Found : N, 15.24. $C_{11}H_{12}N_2O$ requires N, 14.89 per cent.).

Cyan-acetbenzylamide.—In the preparation of this substance, Whiteley's method (*J. Chem. Soc.*, **1921, 119**, 370) for the preparation of malon-di-benzylamide was used.

Ethyl cyanacetate (32 g.) and benzylamine (22 g.) were put in a conical flask and refluxed gently on a sand-bath.

The substance condensed readily to a yellowish white mass. The heating was stopped after seven hours and the solid was washed with a mixture of benzene and petroleum ether to free it from unchanged reactants. The yield was 90 per cent.

It dissolves readily in benzene, toluene, chloroform, ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, acetone and nitrobenzene; less readily in carbon bisulphide and hot water, and is sparingly soluble in light petroleum, carbon tetrachloride and ether. It was crystallised from benzene in white long needles, m. p. 120°. (Found : N, 16.19. $C_{10}H_{10}N_2O$ requires N, 16.09 per cent.).

Cyanacetmethylamide.—This was prepared by a method corresponding to the method of Whiteley (*loc. cit.*) for the preparation of malon-di-ethylamide, by shaking a mixture of ethyl cyanacetate (50 g.), methylamine (45 g. of 33% solution) and sodium hydroxide (0.2 g.) for about one hour, at 0°, until it was homogeneous. After keeping the mixture at the ordinary temperature for twelve hours the solution was concentrated on a water-bath. On cooling, a reddish pasty mass was obtained. It was drained on a porous plate when a mass of granular solid was obtained. The yield was very poor being about 25 per cent.

It is very soluble in methyl alcohol, ethyl alcohol, chloroform, ethyl acetate, acetic acid, acetone, water and nitrobenzene; less soluble in benzene and toluene; and sparingly soluble in carbon tetrachloride, carbon bisulphide, ether and petroleum. It crystallises in long white needles from benzene, m. p. 101°. (Found : N, 28.85. $C_4H_6N_2O$ requires N, 28.57 per cent.).

Cyanacet-ethylamide.—Ethyl cyanacetate (23 g.) was condensed with ethylamine (38 g. of 33 per cent solution) in the same way as cyanacetmethylamide. The yield was about 15 per cent.

It is readily soluble in chloroform, ethyl acetate, acetic acid, methyl alcohol, ethyl alcohol, water, acetone and nitrobenzene; less readily in benzene and toluene; and sparingly soluble in carbon tetrachloride, carbon bisulphide, ether and light petroleum. It was crystallised from benzene as white needles, m. p. 74°. (Found: N, 25·21. $C_5H_8N_2O$ requires N, 25·0 per cent.).

We take this opportunity to record our thanks to the Government of H. H. The Maharaja Gaekwar of Baroda for a grant which has defrayed the expense of this investigation.

Chemistry Department,
The College, Baroda.

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XII—Interaction of Chlorosulphonic Acid with Substituted Amides of Cyanacetic Acid.

BY K. G. NAIK AND M. B. AMIN.

The aim with which this piece of work was undertaken was to study the reactivity of the two hydrogen atoms of a reactive methylene group situated between a cyanogen group and a carbonyl group, as in the case of substituted amides of cyanacetic acid. Attempts were already made to study the reactivity in the case of substituted amides of malonic acid using sulphur monochloride and sulphur dichloride as reagents by Naik (*J. Chem. Soc.*, 1921, **119**, 379, 1231), by Naik and Avasare (*ibid*, 1922, **121**, 2592, 2595), by Naik and Patel (*J. Indian Chem. Soc.*, 1924, **1**, 27), by Naik and Jadhav (J. *Indian Chem. Soc.*, 1926, **3**, 259). Attention is here confined to the study of the interaction of some of the substituted amides of cyanacetic acid using chlorosulphonic acid as the reagent.

It is well-known that chlorosulphonic acid* reacts with many organic compounds giving rise to sulphonic derivatives

In fact the reagent has been often employed in the preparation of such compounds (Thrope's "Dictionary of Applied Chemistry," Vol V. p. 301).

Reference to previous work[1] clearly shows that chlorosulphonic acid was principally used either in sulphonating aromatic compounds or in the preparation of sulphonyl chlorides. It was expected that here, too, the chlorosulphonic acid would attack the hydrogen atoms of the reactive methylene group and give rise to sulphonic acid derivatives. The experimental evidence recorded in this paper bears this out.

An attempt is also made here to shew that the reactivity of these hydrogen atoms depends, in some measure, on the sumtotal negativity of the groups adjoining the reactive methylene grup.

Interaction of chlorosulphonic acid with the following substances was studied :—

Cyanacetanilide;	cyanacet-benzylamide;
cyanacet-*p*-toluidide;	cyanacet-α-naphthylamide;
cyanacet-*o*-toluidide;	cyanacet-β-naphthylamide;
cyanacet-*m*-toluidide;	cyanacet-xylidide (1:4:5).

The first sulphonic acid of the series enumerated above was prepared by reacting cyanacetanilide with chlorosulphonic acid, using dry salicyl chloroform prepared according to Anschütz's method (*Annalen*, 1893, **273**, 94; *Ber.*, 1892, **25**, 3501, 3512), as the medium of interaction. Salicyl chloroform, so prepared, has no action on chlorosulphonic acid at its boiling point.

[1] Hemilian (*Ber.*, 1873, 6, 196); Claessen (*Ber.*, 1881, 14, 307); Hodgkinsen and Mathews (*Ber.*, 1883, 16, 1103); Limpricht (*Ber.*, 1885, 18, 2172); Traube (*Ber.*, 1890, 23, 1634); Reinhard (*J. pr. Chem.*, 125, 332.; Stewart (*J. Chem. Soc.*, 1923, 123, 2384, 2388); Jacob, Pollak. Funeggand Reiz (*Monatsh.* 1926, 46, 383, 397); Krasjinovic (*Ber*, 1926, 59, 2117, 2719).

During the course of the interaction, neither sulphonyl chlorides nor sulphones of the aromatic substituted amides of cyanacetic acid could be isolated. In all the cases sulphonic acid derivatives were obtained and the reagent attacked the methylene group.

Cyanacetanilide, readily interacted with chlorosulphonic acid, thus:

$$CN{\cdot}CH_2{\cdot}CONHPh + 2ClSO_3H = CN{\cdot}C(SO_3H)_2{\cdot}CONHPh + 2HCl.$$

(I)

That the constitution assigned to (I) is correct, and that all the sulphoacids, derived from the various amides enumerated above, can be generally so represented follows from the considerations given below.

(1) That the hydrogen atoms eliminated during the course of the interaction are not those which were originally attached to the nucleus because on hydrolysis with alcoholic caustic potash, *p*-toluidine was obtained as one of the products of hydrolysis from the corresponding sulpho-acid which was derived from cyanacet-*p*-toluidide.

(2) The results of the above hydrolysis also point to the fact that the hydrogen atoms replaced by the sulphonic groups are not those which were originally attached to the nitrogen atoms, as in that case, *p*-toluidine could not have been found as one of the products of hydrolysis.

(3) Further, on attempting to brominate the sulpho-acid (I) the two HSO_3 groups were found to have been replaced by two bromine atoms, as was apparent from subsequent reduction of the di-bromo derivative, both the bromine atoms being easily reduced by Kurt Meyer's method. This clearly proves that the bromine atoms were attached to the methylene carbon atom, and hence, the original sulphonic groups which were replaced by these bromine atoms, also had been attached to the methylene cardon atom.

The three cyanacet-toluidides, cyanacet-benzylamide and cyanacet xylidide and cyanacet-naphthylamides react in a similar manner with chlorosulphonic acid giving analogous sulphonic acid derivatives. But in the cases of the naphthylamides a longer time was required before the reaction was complete.

In relation to the question of the reactivity of the hydrogen atoms of the methylene group with regard to chlorosulphonic acid it may be said that the experimental observations afford a clear evidence that the avidity of the interaction of chlorosulphonic acid with the substituted amides depends on the total negativity of the groups attached to the two remaining valencies of the methylene carbon atom. In the case of cyanacetamide in which one of the valencies of the methylene carbon atom carries the neutral group, ($-CONH_2$), no reaction takes place. But when the neutral character of this group is disturbed by the entrance in it of a phenyl, a tolyl, a benzyl, a naphthyl or a xylyl group, the reactivity starts.

Although no definite measurements have been made, it is evident from the experiments recorded here, that the rapidity with which the reaction proceeds in these cases depends on the electro-negative character of the groupings attached to the methylene carbon atom. Thus in a series like this—

(1) $CN{\cdot}CH_2{\cdot}CONH_2$, (2) $CN{\cdot}CH_2{\cdot}CONHC_6H_5$,
(3) $CN{\cdot}CH_2{\cdot}CONHC_7H_7$ (4) $CN{\cdot}CH_2{\cdot}CONHC_8H_9$,
(5) $CN{\cdot}CH_2{\cdot}COOEt$,

the reactivity which is absent in (1), starts with (2), and goes on increasing through the series.

The mechanism of the interaction studied here is interesting. In such cases where both the hydrogens of the methylene group are replaced by sulponic groups when the reaction starts, the substance may be supposed to assume an enolic form (Norris and Thorpe, J. *Chem. Soc.*, 1921, **119**, 1203).

Experimental.

Disulphocyanacetanilide:—Cyanacetanilide (3 g.) was mixed in a flask with 25 c. c. of salicyl chloroform and an excess of chlorosulphonic acid (5 g.) was added. A vigorous reaction started with evolution of heat and hydrogen chloride. The flask was kept overnight and refluxed the next day in order to complete the reaction. When the evolution of hydrogen chloride ceased and the superfluous chloroform was taken out, 100 c. c. of distilled water were added to the syrupy product and the mixture was boiled. The syrupy mass went into solution and was finally filtered to free it from any unaltered cyanacetanilide. The filtrate deposited shining leaflets, which were washed repeatedly with alcohol in which they were almost insoluble. Finally the product was recrystallised from water. During the course of this investigation it was observed that in all the cases molecular proportions of the reactants did not give a good yield of the final product. An excess of chlorosulphonic acid gave quite satisfactory results, the chance of the amide remaining unreacted being thus completely eliminated.

The pure substance was found to be almost insoluble in alcohol, chloroform, carbon disulphide, carbon tetrachloride, acetone, benzene, toluene, ether and light petroleum. It was extremely soluble in hot water. It had no m.p. but charred above 270°. (Found : S, 16·06; H_2O, 18·3; N, 7·65; Eqv. wt., 197. $C_9H_8O_7N_2S_2,4H_2O$ requires S, 16·32; H_2O, 16· 6; N, 7·16 per cent. Equiv. wt, 196.)

In the following preparations 5 g. of chlorosulphonic acid and 3 gms. of the substituted amides were employed. The products were purified as in the previous case. In solubility and other physical properties they resembled disulphocyanacetanilide.

Disulphocyanacet-p-*toluidide*, crystallised from water in colourless shining leaflets. It had no definite m.p. but darkened and charred at about 270°. Water of crystallisation = $2H_2O$, of which the compound loses half a molecule of

water (2.91 per cent.) at 120°. (Found : S, 17.1, $C_{10}H_{10}O_7N_2S_2.2H_2O$ requires S, 17.29; loss of water, 2.43 per cent.)

Disulphocyanacet-o-*toluidide* had no definite m. p. but charred at 255-265°. (Found : S, 17.0 $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17.29 per cent.).

Disulphocyanacet-m-*toluidide* crystallised in colourless shining scales. It has no definite m. p. but chars between 260° and 270°. (Found : S, 16.96. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17.29 per cent.).

Disulphocyanacet-∝-naphthylamide crystallised from hot water. It has no definite m. p. but chars between 270° and 280°. (Found: S, 16.46. $C_{13}H_{10}O_7N_2S_2$, H_2O requires S, 16.49 per cent.).

Disulphocyanacet-β-naphthylamide was purified by crystallisation from hot water. It formed shining yellowish stout needles, which had no definite m. p. but charred between 270° and 280°. (Found : S, 15.80. $C_{13}H_{10}O_7N_2S_2,H_2O$ requires S, 16.49 per cent.).

Disulphocyanacetbenzylamide formed colourless plates, which charred between 265° and 275°. (Found: S, 17.3. $C_{10}H_{10}O_7N_2S_2,2H_2O$ requires S, 17.29 per cent.).

Disulphocyanacetxylidide (1:4:5) crystallised in the form of colourless light shining scales. It has no definite m. p. but chars between 270° and 280°. (Found: S, 17.4. $C_{11}H_{12}O_7N_2S_2,2H_2O$ requires S, 17.18 per cent.).

The authors desire to express their gratitude to His Highness the Maharaja Gaekwar's Government for placing at their disposal the resources of the Research Laboratory of the Baroda College and defraying all the expense incurred in connection with this investigation.

Chemistry Department,
The College Baroda.

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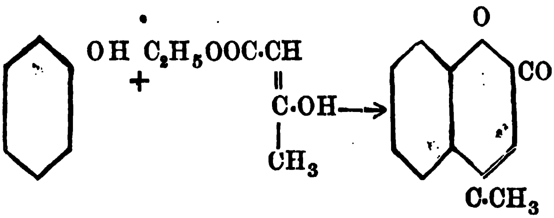
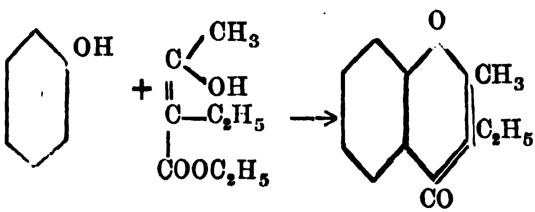
Studies in Coumarin Condensations. Part I. The Condensation of *Allylacetoacetic Ester with Phenols.*

BY KUVERJI GOSAI NAIK, RANCHHODJI DAJIBHAI DESAI AND HARIBHAI RANCHHODJI DESAI.

Though ethyl acetoacetate condenses with phenols to give coumarins (I) * Simonis and his co-workers have shewn that ethylacetoacetic ester condenses with phenols in presence of phosphorus pentoxide to form benzo-γ-pyrones (II):



(I)



(II)

According to Ghosh and Jacobson (*J. Chem. Soc.*, 1915, **107**, 424, 959, 1051), the formation of either the benzo-α-pyrones (coumarins) or the benzo-γ-pyrones mainly depends upon the character of the radical present in the substituted acetoacetic esters, whereas the condensing agent plays a subsidiary part. Thus, even using concentrated sulphuric acid as the condensing agent, the acetoacetic esters of the general formula, $CH_3{\cdot}C(OH)=CR{\cdot}COOC_2H_5$ give the benzo-γ-pyrones, where R is the benzyl or phenyl group. If R is

* Pechmann, *Ber.*, 1884, 17, 929, 1646, 2187; 1899, 32, 3681; 1901, 34, 423; Fries and Klostermann, *Annalen*, 1908, 361; Simonis *Ber.*, 1913, 46, 2014; 1914, 47, 2229).

ethyl, a mixture of α- and γ-pyrones is obtained, while only coumarins are obtained if R is either hydrogen or methyl. This work of Ghosh and Jacobson has been contradicted by Baker (*J. Chem. Soc.*, 1925, **127**, 2349) and Baker and Robinson (*J. Chem. Soc.*, 1926, **129**, 1981) and they are of opinion that all the products prepared by Ghosh and Jacobson are benzo-α-pyrones and not benzo-γ-pyrones. Thus the available views regarding the influence of the radical present in the methylene group of the acetoacetic ester are conflicting.

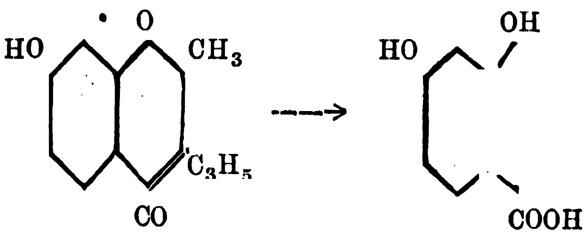
On consulting the literature, it was found that the effect of an alkyl radical containing more than two carbon atoms, such as propyl, butyl, etc. and an unsaturated alkyl radical, such as allyl, substituted in place of one of the hydrogens in the methylene group of the acetoacetic ester, on the course of the reaction between the phenols and such esters, has not been fully and systematically studied. This communication describes the results of the condensation of various phenols with allyl acetoacetic ester, using concentrated sulphuric acid as the condensing agent.

Phenol, resorcinol, pyrogallol, *m*-cresol, α-naphthol, β-naphthol, phloroglucinol, guaiacol, thymol, catechol, and quinol were condensed with the above ester. Phenol, however, failed to give any solid product; α-naphthol condensed very easily giving almost a quantitative yield of 4-methyl-3-allyl-5:6-naphtho-pyrone. The phenols, having a substituent in the *meta*-position, *e.g.*, resorcinol, *m*-cresol, and phloroglucinol condensed very readily giving almost quantitative yields of the corresponding coumarins. Pyrogallol condensed with the ester giving the α-pyrone when phosphorus oxychloride was used as the condensing agent. Catechol, guaiacol, thymol, β-naphthol and quinol did not condense at all.

The condensation of resorcinol with the ester was also carried out using gaseous hydrochloric acid as the condensing agent. The reaction proceeded very readily in the cold, and a product containing chlorine was obtained. The acetyl

and benzoyl derivatives also contain chlorine. The constitution 7-hydroxy-3-chloropropyl-4-methyl-benzo-∝-pyrone has been provisionally assigned to this compound.

When coumarins, obtained from resorcinol and ∝-naphthol, were subjected to the action of 50% boiling aqueous solution of sodium hydroxide (4 hours), and the solution was acidified, the original products were obtained in each case. If the products were benzo-γ-pyrones, resorcylic acid and naphthol-carboxylic acid respectively would result:



The benzo-γ-pyrones are known to give the hydroxy carboxylic acids on hydrolysis (Ghosh and Jacobson, *loc. cit.*), but the ∝-pyrones may or may not give them. As the carboxylic acids were not obtained in the present case, the ∝-pyrone constitution has been suggested for them.

Experimental.

7-Hydroxy-3-allyl-4-methyl-benzo-∝-pyrone.—To a mixture of resorcinol (2 g.) and allylaceto-acetic ester (3 g.) concentrated H_2SO_4 (20 g.) was added in small amounts. It was found necessary to keep the mixture cool. It was kept overnight and then poured into a large amount of water. A pale-brown solid separated, which was filtered off and dried (yield, 3·8 gms.). When the crude substance was boiled with alcohol, it became white, and melted at 221°-222°. It is sparingly soluble in alcohol and glacial acetic acid. It was recrystallised from a mixture of pyridine and water, when it was obtained in small white needles. The substance for analysis was dried in an air-oven at 120°. (Found: C, 72·09; H, 5·79. $C_{13}H_{12}O_3$ requires C, 72·22; H, 5·55 per cent.).

The *acetyl derivative* was prepared by boiling the substance with acetic anhydride for an hour. When crystallised from alcohol, white plates melting at 152°-153° were obtained, (Found: C, 74·88; H, 4·89, $C_{20}H_{16}O_4$ requires C, 75·0 and H, 5·0 per cent.)

Hydrolysis of 7-Hydroxy-3-allyl-4-methyl-benzo-α-pyrone.—The substance (1 g.) was boiled with 15 c.c. of 50% aqueous caustic potash for four hours. The clear solution was crystallised from pyridine and water. It was found to be the original substance, as was apparent from its m.p. and its acetyl derivative.

7-Hydroxy-3-chloropropyl-4-methyl-benzo-α-pyrone.—Resorcinol (2 g.) and allylacetoacetic ester (3 g.) were dissolved in 10 c.c. of glacial acetic acid. Dry gaseous hydrogen chloride was passed into the mixture for two hours. As the mixture became hot, the flask had to be cooled under water. After an hour, the mixture became viscid, and on keeping overnight, white crystalline plates separated out. On diluting the mixture with water, more of the substance separated (yield, 4 gms.). The product which crystallised from alcohol in white, prismatic needles, melted at 200°-201°. The chlorine in it was not removed even by boiling its alcoholic solution with sodium acetate solution. (Found: Cl, 14·05. $C_{13}H_{13}O_3Cl$ requires Cl, 14·06 per cent.).

The *acetyl derivative* prepared as above, crystallised from alcohol in white, short needles melting at 122°-123°. (Found: Cl, 12·28. $C_{16}H_{15}O_4Cl$ requires Cl, 12·05 per cent).

The *benzoyl derivative* crystallised from glacial acetic acid in white, shining needles melting at 193°. (Found: Cl, 10·15. $C_{20}H_{17}O_4Cl$ requires Cl, 9·96 per cent.).

3-Allyl-4-methyl-5 : 6-naphtho-α-pyrone.—A mixture of α-naphthol (2 g.) and allylacetoacetic ester (2 g.) was treated with concentrated H_2SO_4 (20 g.). After keeping the mixture

overnight, it was poured into water (yield, 3 gms.). After treatment with animal charcoal in alcoholic solution the substance was obtained as yellowish white plates, m. p. 155°-156°. (Found : C, 81·33; H, 5·65. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6 per cent.).

3-*Allyl*-4 : 7-*dimethyl-benzo-∝-pyrone*.—This was prepared as usual from *m*-cresol (3 g.) allylaceto-acetic ester (3 g.) and concentrated H_2SO_4 (10 gm.) (yield, 3·2 gms). Recrystallisation from alcohol gave yellowish white plates, m. p. 126°-127°. (Found : C, 78·24; H, 6·65. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·54 per cent.).

5 : 7-*Dihydroxy*-3-*allyl*-4-*methyl-benzo*-∝-*pyrone*.—This was prepared in a manner similar to the above, from anhydrous phloroglucinol (1·5 g.), allyl acetoacetic ester (1·5 g.) and concentrated H_2SO_4 (10 gm.) (yield, 2 gms.). The pale yellow powder was recrystallised from dilute acetic acid, when pale brown, silky needles, m. p. 207°-208° were obtained. It is very soluble in alcohol, acetone and glacial acetic acid, but sparingly soluble in benzene and petroleum. (Found: C, 66·75; H, 5·50. $C_{13}H_{12}O_4$ requires C, 67·24 and H, 5·17 per cent.).

The *acetyl derivative* crystallises from alcohol in white plates, m. p. 130°-131°. (Found: C, 64·25; H, 5·61. $C_{17}H_{16}O_6$ requires C, 64·56; H, 5·28 per cent.)

7:8-*Dihydroxy*-3-*allyl*-4-*methyl-benzo*-∝-*pyrone*.—This could not be obtained by using H_2SO_4 as a condensing agent. A mixture of pyrogallol (2 g.), allylacetoacetic ester (2 g.) and phosphorus oxychloride (1·5 g.) was heated on a water-bath for nearly an hour. Copious fumes of hydrogen chloride were evolved. After the reaction was over, the viscous mass was poured into water. Recrystallisation from dilute acetic acid gave white, small plates melting at 175°-176° (yield, 2·5 gm). (Found: C, 66·87; H, 5·23. $C_{13}H_{12}O_4$ requires C, 67·24; H, 5·17 per cent.)

The *acetyl derivative* crystallises from alcohol in white, prismatic needles, m. p. 145°-146°. (Found: C, 64·12; H, 5·51, $C_{17}H_{16}O_6$ requires C, 64·56; H, 5·28 per cent.).

We desire to express our gratitude to the Government of His Highness the Maharaja Gaekwar, for a grant which has defrayed the expenses incurred in this research.

The Chemistry Department.
The Colleges Baroda.

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XIV—Phosphorus Oxychloride as a Condensing Agent in the Synthesis of Coumarin Derivatives.

By K. G. Naik, R. D. Desai and R. K. Trivedi.

The subject of the present communication arose from an attempt to condense benzylacetoacetic ester with β-naphthol in presence of concentrated sulphuric acid as the condensing agent. The expected coumarin 3-benzyl-4-methyl-1 :2-β-naphthopyrone was not obtained, but methylindene-carboxylic acid was produced by the internal condensation of the ester. ∝-Naphthol was however, condensed under identical conditions by Ghosh and Jacobson to give the corresponding pyrone derivative (*J. Chem. Soc.*, 1915, **107**, 424). But on repeating the condensation under the conditions outlined therein, we failed to get the product obtained by them. When concentrated sulphuric acid was replaced by phosphorus oxychloride as the condensing agent, ∝-naphthol condensed very readily with benzylacetoacetic ester giving the coumarin derivative.

Equimolecular quantities of the phenol and, benzylacetoacetic ester were mixed with phosphorus oxychloride (about 0·5 gm, for 2 gms. of the mixture) and the whole heated on the water-bath for about an hour. The mixture was then poured into water, when a solid product separated which was subsequently purified from alcohol.

In each case, excellent yields of crystalline products were obtained. From the physical properties and the melting points of their derivatives, as shown in the adjoining table, the produts appeared to be identical with those of Ghosh and Jacobson.

Products obtained from various phenols and benzyl-acetoacetic ester.

	Phenols.	Resorcinol.	α-Naphthol.	Pyrogallol.	Phloro-glucinol.
Observations by Ghosh & Jacobson.	Crystalline form	Short, yellow glistening prisms.	Yellow needles.	—	Hard, short needles.
	M.p. ...	224°	187°	185°	218°
	M.p. of acetyl derivative...	168°	—	172°	154°
	M.p. of benzoyl derivative.	150°	—	184°	—

	Phenols.	Resorcinol.	α-Naphthol.	Pyrogallol.	Phloro-glucinol.
Observations by the authors.	Crystalline form	Colourless, glistening prisms.	Pale yellow, slender needles.	Colourless, glistening plates.	Short needles.
	M.p. ...	225°	189°-90°	193°	227°
	M.p. of acetyl derivative...	171°	—	172°	158°-59°
	M.p. of benzoyl derivative.	160°	—	181°	124°-25°

The College, Baroda,

(Reprinted from the Journal of the Indian Chemical Society, Vol, VI. Issue No. 5.)

XV-Interaction of Chlorosulphonic Acid with the Substituted Amides of Malonic and Methylmalonic Acids.

By K. G. Naik and C. H. Shah.

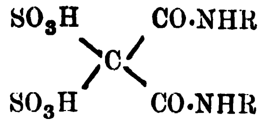
The investigation which forms the subject of this communication was undertaken with a view to study the reactivity of the two hydrogen atoms of a reactive methylene group situated between two carbonyl groups, $—CO·CH_2·CO—$, as in the case of the substituted amides of malonic acid. Reference is invited to a previous communication by Naik and Amin (J. *Indian Chem. Soc.*, 1928, **5**, 579). Attention is here confined to the study of the interaction of some of the substituted amides of malonic acid using chlorosulphonic acid as the reagent. For this purpose the interaction of chlorosulphonic acid with the following substances was studied :—

(1) Malon-diphenylamide, (2) Malon-dibenzylamide, (3) Malon-di-*p*-tolylamide, (4) Malon-di-*o*-tolylamide, (5) Malon-di-*m*-tolylamide, (6) Malon-di-α-naphthylamide, (7) Malon-di-β-naphthylamide, (8) Malon-di-(1 : 3 : 4)-xylidide, (9) Malon-dipropylamide, (10) Malonmono-*p*-tolylamide, (11) Methylmalon-diphenylamide, (12) Methylmalon-di-*p*-tolylamide, (13) Methylmalon-di-*o*-tolylamide, (14) Methylmelon-di-*m*-tolylamide, (15) Methylmalon-di-α-naphthylamide, (16) Methylmalon-di-β-naphthylamide, (17) Methylmalon-di-(1 : 3 : 4)-xylidide.

Of the above, compounds, 8, 15, 16 and 17 were prepared for the first time, by the same method as that used for preparing the corresponding amides of malonic acid.

The results of the present investigation could be summarised as under :—

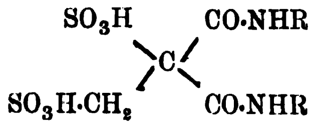
Type I. Compounds (1) to (10), with the exception of (9), react to form disulpho-compounds whose constitution can be generally represented as :—



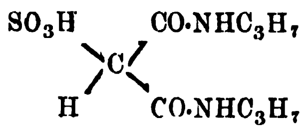
(I)

(R = phenyl, benzyl, tolyl, naphthyl, or xylyl group).

Type II. Compounds (11) to (17) give rise to disulpho-derivatives, which can generally be represented as :—



Compound (9) reacts with chlorosulphonic acid to form a derivative which can be represented as :—



That the constitution assigned to (I, R = Ph) is correct and that all the sulpho-acids, derived from the various amides enumerated above, can generally be thus represented, follows from the following considerations :—

(*i*) That the hydrogen atoms attacked by the chlorosulphonic acid are not eliminated from the phenyl groups or any such analogous nucleus becomes evident from the course of the reaction in the case of malon-dipropylamide where no such aromatic nuclei are present, and yet the sulpho-acid is produced.

(*ii*) That the hydrogen atoms eliminated were not those which were originally attached to the two nitrogen atoms, because only one sulpho-group enters in malon-dipropylamide, though there are two symmetrically situated —NH— groups present in it.

The compounds enumerated under type (I) reacted similarly with chlorosulphonic acid. Only in the case of malon-di-α-naphthylamide, a longer time was required before the reaction was complete.

In the above cases, molecular proportions of the reacting substances did not give a good yield of the sulpho-acids and much of the amide remained unaltered. When they were taken in equal quantities, the yield improved and the products were obtained in a purer state.

With a view to study the stability of the two sulphonic acid groups, attached to the methylene carbon atom, it was thought desirable to see how far these groups could be replaced by a negative group, such as the nitro-group.

The following four compounds were, therefore, subjected to a process of nitration :—

(1) Disulpho-malon-diphenylamide;
(2) Disulpho-malon-di-*p*-tolylamide;
(3) Disulpho-malon-di-*o*-tolylamide;
(4) Sulphomethyl-sulphomalon-diphenylamide.

Compounds (2) and (3) when treated with dilute nitric acid yielded dinitro-derivatives, thus :—

$$(HSO_3)_2 : C : (CO{\cdot}NHC_7H_7)_2 \xrightarrow{HNO_3} (NO_2)_2 : C : (CO{\cdot}NHC_7H_7)_2$$

o - and *p* -

Compounds (1) and (4) on being nitrated gave tetranitro-derivatives. Thus in the case of (1) the reaction followed the course as under :—

$$(HSO_3)_2:C:(CO{\cdot}NHC_6H_5)_2 \xrightarrow{HNO_3} (NO_2)_2:C:(CO{\cdot}NHC_6H_4NO_2)_2.$$

The tetranitro-derivative obtained from disulpho-malon-diphenylamide was hydrolysed with 50 per cent. aqueous caustic potash solution, thus :—

$$(NO_2)_2:C:(CO{\cdot}NHC_6H_4{\cdot}NO_2)_2 + 2KOH = (NO_2)_2:(C:(CO_2K)$$
$$+ 2C_6H_4(NH_2)NO_2.$$

The formation of potassium dinitro-malonate as above shows that the two —SO_3H groups originally present in disulpho-amide, were replaced by the nitro-groups, the other two being present in the aromatic nuclei of the above amide. Both the sulpho-groups seem to have been simultaneously replaced by the two nitro-groups.

EXPERIMENTAL.

A general method of preparing the sulpho-acide is to add equal quantities of the amide and chlorosulphonic acid to dry chloroform in a conical flask. When properly mixed the reaction starts and proceeds vigorously with much evolution of heat. Clouds of hydrogen chloride are thrown out in the initial stage of the reaction. The flask is kept normally cool by holding under a water-tap. Subsequently, the mixture is refluxed on a sand-bath for two hours. when the evolution of hydrogen chloride stops. The solvent is then removed and the red syrupy reaction product poured into 100 c.c. of water. The syrupy mass goes into solution. On concentration and cooling, the sulpho-acid separates out in clusters of shining leaflets.

Disulpho-malon-diphenylamide.—It was obtained from malondiphenylamide (3 g.) and chlorosulphonic acid (3 g.) in 20 c.c. of chloroform. It formed shining colourless leaflets, soluble in water, and insoluble in alcohol, acetone, acetic acid, benzene, toluene, carbon disulphide, carbon tetrachloride, ether, ethyl acetate, nitrobenzene and light petroleum. It has no definite m. p. but decomposes above 280°. It crystallises out with two molecules of water of crystallisation, which is last when heated to 140–150° for four hours. (Found : S, 14·3; H_2O, 7·6; Equiv. wt., 224. $C_{15}H_{14}O_8N_2S_2,2H_2O$ requires S, 14·2; H_2O, 8·0 per cent, Equiv. wt., 225).

Nitration.—The above disulpho-acid (2 g.) was gradually added to a mixture of 20 c.c. of nitric acid (*d* 1·2) and 20 c.c. of glacial acetic acid. On warming the mixture, oxides of nitrogen began to evolve. The reaction mixture was kept on a water-bath till the evolution of the fumes ceased. Then the remaining fumes of nitrogen peroxide were blown away by air and the mixture poured into water. On concentration, the nitro-compound crystallised out in the form of deep orange crystals, m. p. 124°. The product was found to be

soluble in alcohol, benzene, chloroform, acetone and nitrobenzene. (Found: N, 19·32. $C_{15}H_{10}O_{10}N_6$ requires N, 19·35 per cent.).

Hydrolysis of D*initromalon-dinitrodiphenylamide*.—About 2 g. of the substance were refluxed for several hours with 50 per cent. caustic potash solution and the resulting solution was filtered. The filtrate was concentrated on the water-bath, when potassium dinitromalonate separated out, which was collected, and recrystallised from hot water. (Found: K, 29·02. $C_3O_8N_2K_2$ requires K, 28·88 per cent,.)

The *barium salt*, $Ba(SO_3)_2$:C:$(CO{\cdot}NHC_6H_5)_2,H_2O$, was prepared by digesting an aqueous solution of the acid with barium carbonate. The solution was filtered and the filtrate on being concentrated deposited the barium salt as needle-shaped crystals. (Found: H_2O, 3·09; Ba, 24·41. $C_{15}H_{12}O_8$-N_2S_2Ba,H_2O requires H_2O, 3·17; Ba, 24·2 per cent,).

The *potassium salt*, $(KSO_3)_2$:C:$(CO{\cdot}NHC_6H_5)_2,9H_2O$, was prepared by the action of caustic potash on the solution of the acid. (Found : H_2O, 24·46; K, 11·94. $C_{15}H_{12}O_8N_2S_2K_2$, $9H_2O$ requires H_2O, 24·85; K, 11·96 per cent.).

The *sodium salt*, $(NaSO_3)_2$:C:$(CO{\cdot}NHC_6H_5)_2,3H_2O$, was prepared in a similar way using caustic soda. (Found: H_2O, 10·33; Na, 9·01. $C_{15}H_{12}O_8N_2S_2Na_2,3H_2O$ requires H_2O, 10·54; Na, 8·98 per cent.).

Calcium salt.—It was prepared like the barium salt, and crystallised from alcohol. (Found: Ca, 8·5. $C_{15}H_{12}O_8N_2S_2Ca$, H_2O requires Ca, 8·51 per cent.).

Ammonium salt.—The solution of the acid was just neutralised with ammonium hydroxide and concentrated when it crystallised out in large prisms. (Found: H_2O, 3·84; N, 12·06, $C_{15}H_{20}O_8N_4S_2$, H_2O requires H_2O, 3·86; N, 12·01 per cent.).

Disulphomalon-dibenzylamide.—Two g. of the amide were made to react with 2 g. of the acid in 20 c. c. of chloroform. The reaction product was obtained by a process similar to that followed in the preparation of disulphomalon-diphenylamide. The pure substance was crystallised from distilled water. It had no definite melting point, but decomposed at temperatures above 300°. (Found : H_2O, 3·98; S, 14·08. $C_{17}H_{18}O_8N_2S_2,H_2O$ requires H_2O, 8·61; S, 13·9 per cent.).

The *barium salt*, $Ba(SO_3)_2:C:(CO \cdot NHC_7H_7)_2,\frac{1}{2}H_2O$ was prepared as usual by neutralising the sulpho-acid with barium carbonate. (Found: H_2O, 1·54; Ba, 23·43. $C_{17}H_{16}O_8N_2S_2Ba,\frac{1}{2}H_2O$ requires H_2O, 1·53; Ba, 23·42 per cent.).

Sodium salt.—It was prepared as usual. (Found: Na, 9·44. $C_{17}H_{16}O_8N_2S_2Na_2$ requires Na, 9·46 per cent.).

Potassium salt.—(Found : K, 15·12. $C_{17}H_{16}O_8N_2S_2K_2$ requires K, 15·05 per cent.).

The *ammonium salt*, $(NH_4SO_3)_2:C:(CO \cdot NHC_7H_7)_2,\frac{1}{2}H_2O$ was prepared by neutralisation of the acid with ammonium hydroxide. (Found : H_2O, 1·46; N, 11·31. $C_{17}H_{24}O_8N_4S,\frac{1}{2}H_2O$ requires H_2O, 1·82; N, 11·33 per cent.).

*Disulphomalon-di-*p*-tolylamide.*—The amide (3 g.) was made to react with chlorosulphonic acid (3 g) in 25 c. c, of dry chloroform. The product (which was obtained by the method adopted in the previous cases) was found to be insoluble in all organic solvents. It was soluble only in hot water and had no definite melting point but decomposed at 300°. (Found: S, 14·42. $C_{17}H_{18}O_8N_2S_2$ requires S, 14·47 per cent.).

Hydrolysis.—The above acid (5 g.), was added to a solution of 30 g. of caustic soda in 100 c. c. of alcohol and the whole refluxed for 48 hours. The resulting product was diluted with water and then extracted with ether. The ethereal extract deposited *p*-toluidine after removal of ether.

Nitration.—The acid (1 g.) was added to 20 c. c. of dilute nitric acid. On heating and concentrating the solution, the reaction product was obtained as orange crystals very soluble in alcohol, benzene, acetone and acetic acid but sparingly so in petroleum. It melts at 68°. (Found: N, 14·08. $C_{17}H_{16}O_8N_4$ requires N, 13·86 per cent.)

Disulphomalon-di-o-tolylamide.—Two g. of the amide and 3 g. of chlorosulphonic acid were used. On crystallisation from water the product formed long, silky needles. (Found: S, 14·5. $C_{17}H_{18}O_8N_2S_2$ requires S, 14·47 per cent.).

Potassium salt.—(Found : K, 15·06. $C_{17}H_{16}O_8N_2S_2K_2$ requires K, 15·05 per cent).

Nitration.—The acid, on nitration, as in the case of the *para*-derivative, gave a greenish coloured product, m. p. 85°. (Found: N, 15.1. $C_{17}H_{16}O_6N_4$ requires N, 15·05 per cent.).

Disulphomalon-di-m-tolylamide.—Two g. of the amide and 2 g. of the acid in 20 c. c. of chloroform were taken. The product was obtained from water in white plates. (Found : S, 13·9; H_2O, 3·93. $C_{17}H_{18}O_8N_2S_2,H_2O$ requires S, 13·9; H_2O, 3·91 per cent.).

The *calcium salt* was prepared as usual. (Found: Ca, 8·47. $C_{17}H_{16}O_8N_2S_2Ca$ requires Ca, 8·3 per cent.).

Disulphomalon-di-α-naphthylamide.—This was prepared by allowing 3 g. of the amide to react with 10 g. of the acid in 30 c. c. of chloroform. The product was found to be soluble only in water. (Found : H_2O, 12·92; S, 11·01. $C_{23}H_{18}O_8N_2S_2,4H_2O$ requires H_2O, 12·2; S, 10·92 per cent.).

Disulphomalon-di-β-naphthylamide.—Two g. of the amide were treated with 10 g. of chlorosulphonic acid. The disulpho-derivative was found to be very sparingly soluble in water. It had no definite melting point but decomposed

at 280°. (Found : H_2O, 17·4; S, 10·32. $C_{23}H_{18}O_8N_2S_2,6H_2O$ requires H_2O, 17·36; S, 10·28 per cent.).

Monosulphomalon-dipropylamide.–Two g. of the amide were made to react with 2 g. of the acid. The product could not be isolated in crystalline form, but was obtained as a red syrup. It was soluble in all organic solvents. Its *barium salt* was obtained in the form of large shining leaflets from water. (Found : H_2O, 7·5; Ba, 19·08. $C_{18}H_{34}O_{10}N_4S_2Ba,3H_2O$ requires H_2O, 7·4; Ba, 19·00 per cent.).

*Disulphomalon-mono-*p*-tolylamide.*—This was prepared by treating the mono-amide (2 g.) with chlorosulphonic acid (2 g.) in the usual manner. It was crystallised from water in short needles, (Found: H_2O, 4·93; S, 17·27. $C_{10}H_{12}O_8N_2S_2$, H_2O requires H_2O, 4·8; S, 17·29 per cent.

Disulphomalon-di-(1:3:4)*xyliddie.*—The product from 2 g. of the xylidide and 2 g. of the sulphonic acid separated as white lustrous laminae from hot water. (Found: S, 13·62. $C_{19}H_{22}O_8N_2S_2$ requires S, 13·61 per cent.).

Sulphomethyl-sulphomalon-diphenaylmide.—It was prepared by the interaction of 2 g. of the amide and 2 g. of the acid. It comes out from water in white crystals. (Found: S, 14·94. $C_{16}H_{16}O_8N_2S_2$ requires S, 14·95 per cent.).

Nitration.—The acid was gradually added to a mixture of 20 c.c. of nitric acid (*d* 1·2) and 20 c.c. of acetic acid. After the evolution of the oxides of nitrogen had ceased, it was poured in a small quantity of water, when the nitrated product came out as yellow crystals, m.p. 120°. (Found; N, 18·78. $C_{16}H_{12}O_{10}N_6$ requires N, 18·75 per cent.).

Potassium salt.—(Found: K, 14·97. $C_{16}H_{14}O_8N_2S_2K_2,H_2O$ requires K, 14·94 per cent.),

Sodium salt.—(Found: Na, 9·71. $C_{16}H_{14}O_8N_2S_2Na_2$ requires Na, 9·74 per cent.).

Sulphomethyl-sulphomalon-di-p-tolylamide.—It was obtained in the form of shining needles from hot water. (Found: H_2O, 3·9; S, 13·56. $C_{18}H_{20}O_8N_2S_2$ H_2O requires H_2O, 3·8; S, 13·5 per cent.).

Sulphomethyl-sulphomalon-di-o-tolylamide.—It was obtained from water in white shining crystals, by a process similar to the above, (Found: H_2O, 3·92; S, 13·6. $C_{18}H_{20}O_8N_2S_2,H_2O$ requires H_2O, 3·8; S, 13·5 per cent.).

Potassium salt.—(Found: H_2O, 6·4; K, 13·71. $C_{18}H_{18}O_8$-$N_2S_2K_2,2H_2O$ requires H_2O, 6·33; K, 13·73 per cent.).

Sulphomethyl-sulphomalon-di-m-tolylamide was prepared in the usual way, from methylmalon-di-*m*-tolylamide. (Found: S, 14·12. $C_{18}H_{20}O_8N_2S_2$ requires S, 14·03 per cent.).

Sulphomethyl-sulphomalon-di-α-naphthylamide.—It was obtained from 2 g. of the amide and 10 g. of chlorosulphonic acid, (Found: H_2O, 14·54; S, 10·37. $C_{24}H_{20}O_8N_2S_2,5H_2O$ requires H_2O, 14·56; S, 10·36 per cent.).

Sulphomethyl-sulphomalon-di-β-naphthylamide was obtained in a similar way. (Found: H_2O, 9·4; S, 11·01. $C_{24}H_{20}O_8$-N_2S_2, $3H_2O$ requires H_2O, 9·28; S, 10·99 per cent.).

Sulphomethyl-sulphomalon-di-(1:3:4)*xylidide* was obtained in the form of white scales. (Found: S, 13·24, $C_{20}H_{24}O_8$ N_2S_2 requires S, 13·22 per cent.).

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Chemistry Department,
The College, Baroda.

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XV-(A)—Properties of Conjugated Compounds. Part X Variability in the Mode of Ester Addition to Butadiene Esters and Ketones.

By Ernest Harold Farmer and Thakorbhai Naranji Mehta.

An examination of the additive behaviour of butadienoid compounds with bromine and hydrogen has established that the mode of addition varies from member to member of a conjugated series for the same addendum, the variation being apparently directly related to (although, so far as has been definitely proved, possibly not entirely dependent on) the nature and position of the substituents in the butadiene chain. There is no reason to suppose that dependence of additive mode on the constitution of the conjugated compound does not hold for all the common dividing addenda and consequently it would be expected that the union of sodioesters with butadiene esters would yield $\alpha\beta$-, $\alpha\delta$-, or *both* $\alpha\beta$- and $\alpha\delta$- addition products in different instances. Yet, although the separate occurrence of $\alpha\beta$- and of $\alpha\delta$-addition to butadiene esters (δ-phenylated and δ-alkylated respectively)[1] has been known for more than twenty years (Vorländer, *Annalen*, 1906, **345**, 227), no single instance has been discovered in which *both* $\alpha\beta$- and $\alpha\delta$-addition compounds are simultaneously produced from the same reactants.

Kohler and Butler (*J. Amer. Chem. Soc. 1926* **48**, 1036) and Farmer and Healey (J., 1927, 1060) independently subjected the malonic ester addition products of methyl β-vinylacrylate and methyl sorbate to ozonolytic degradation in order to discover whether $\alpha\delta$-products were indeed the only ones

[1] Indirect evidence as to the possibility of bringing about $\alpha\delta$-ester addition to a phenylated butadiene ester is furnished by Meerwein's production of a double addition product $Ph{\cdot}CHX{\cdot}CH_2{\cdot}$ ${\cdot}CHX{\cdot}CH(CO_2R)_2$ [$X=(CHCO_2R)_2$] from cinnamylidenemalonic ester and sodio-malonic ester, or directly from cinnamaldehyde and sodio-malonic ester. (*Annalen*, 1908, **360**, 324). Here presumably the $\alpha\delta$ addition to the conjugated ester which is first effected is rapidly followed by $\beta\gamma$, $\alpha\beta$-double bond displacement and $\alpha\beta$ addition.

formed, and in 1924, before ozone was available as a reagent in the laboratory, one of the present authors oxidised large quantities of the latter product with permanganate in the hope of isolating tricarballylic acid, the expected degradation product of an $\alpha\beta$-additive compound (unpublished work). The result of these efforts made it appear probable that only $\alpha\delta$-derivatives were formed in these instances, although, in connexion with the compound from methyl sorbate, Kohler and Butler (*loc. cit.*, p. 1045) mention a small fraction of the major degradation product which, differing slightly in boiling point from the remainder, could possibly be derived from the $\alpha\beta$-compound. Similarly the same two conjugated esters appeared to yield only $\alpha\delta$-addition products with methylcyanoacetic ester (Farmer and Healey *loc. cit.*). Since that time the addition of malonic ester to two conjugated ketones has been studied by one of the authors, but in neither case was the simultaneous formation of both $\alpha\beta$- and $\alpha\delta$-products proved.

Now, the ozonolytic degradation of unsaturated ester-addition products usually proceeds so smoothly that the failure to detect thereby the formation of more than one type of additive compound in each instance has suggested that a second type, if produced at all, could represent only an extremely small fraction of the addition product Yet it appeared quite certain from experience gained with other addenda that, if simultaneous formation of $\alpha\beta$ and $\alpha\delta$-compounds could occur at all, then, in some examples at least, the minor component of the addition product should be present to the extent of considerably more than a mere trace. Therefore, whilst the investigation of a sufficiently large number of examples by the degradation methods hitherto employed might ultimately be expected to disclose instances of multiple-type addition (instances in which the $\alpha\beta$-, $\alpha\delta$-ratio approached unity), there seemed to be no question as to the desirability of re-examining some of the older examples by supplementary experimental methods. The

authors have therefore returned to the investigation of the product derived by the interaction of methyl sorbate and methyl sodiomalonate, substituting a reduction process for the degradative methods previously employed.

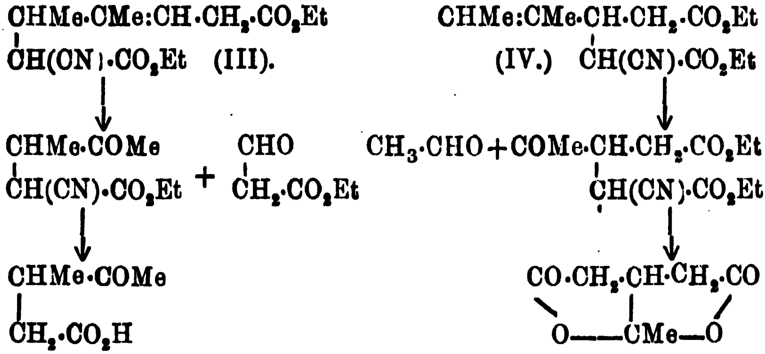
When this product is successively reduced, hydrolysed, and partly decarboxylated, an oily mixture of acids is obtained which is partly separable into its components by distillation. The higher-boiling portion, which quickly solidifies, is β-methylpimelic acid derived from the preponderating $\alpha\delta$-product (I). The lower-boiling portion, which remains liquid, is a mixture of β-methylpimelic acid and β-propylglutaric acid, the latter derived from an $\alpha\beta$-product (II).

$$\begin{array}{ll} \mathrm{CHMe{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CO_2Me} & \mathrm{CHMe{:}CH{\cdot}CH{\cdot}CH_2{\cdot}CO_2Me} \\ \mid & \qquad\qquad\;\;\mid \\ \mathrm{CH(CO_2Me)_2} \quad (\mathrm{I.}) & \qquad\qquad\mathrm{CH(CO_2Me)_2} \quad (\mathrm{II.}) \\ \quad\downarrow & \qquad\qquad\quad\downarrow \\ \mathrm{HO_2C{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H} & \mathrm{HO_2C{\cdot}CH_2{\cdot}CHPr^a{\cdot}CH_2{\cdot}CO_2H} \\ \qquad\qquad\downarrow & \qquad\qquad\quad\downarrow \\ \mathrm{CH_2}{<}\begin{matrix}\mathrm{CHMe{\cdot}CH_2} \\ \mathrm{CH_2{-}CH_2}\end{matrix}{>}\mathrm{CO} & \mathrm{Pr^aCH}{<}\begin{matrix}\mathrm{CH_2{\cdot}CO} \\ \mathrm{CH_2{\cdot}CO}\end{matrix}{>}\mathrm{O} \end{array}$$

The components of this mixture may be readily separated by taking advantage of the dissimilar character of their anhydrides; the unimolecular anhydride of the propylglutaric acid distils at a temperature lower than that at which the polymolecular anhydride of its isomeride begins to suffer degradation to β-methyl*cyclo*-hexanone. Since the propylglutaric anhydride is a liquid and the corresponding acid very difficult to recrystallise, the former is converted into its anilic acid for the purpose of estimating the yield. From the yields so determined with fairly large quantities of material, it appears that $\alpha\beta$-addition accompanies $\alpha\delta$-addition to the extent of at least 7% but improbably more than 10%.

Ethyl γ-methylsorbate also gives both $\alpha\beta$- and $\alpha\delta$-addition products with ethyl sodiocyanoacetate. In this, the latest instance studied, the authors were quite unable to bring about the catalytic reduction of the addition com-

pounds (III and IV) or their closely related derivatives. But here degradation by ozonolysis yields definite evidence. The mixture of ester-addition products gives the appropriate fission products according to the scheme:



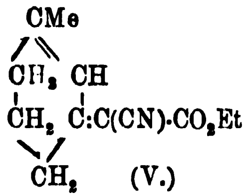
Owing to the failure of the reduction method a satisfactory estimate of the $\alpha\beta$, $\alpha\delta$-ratio could not be made, but it was clear from the amounts of the different degradation products isolable that the ratio approached unity far more closely than in the preceding example.

The addition of ethyl malonate and of ethyl cyanoacetate to ethyl $\beta\delta$-dimethylsorbate has been attempted, but here, as with ester addition to ethyl crotylidenemalonate (Farmer and Healey, *loc. cit.*), conditions suitable for promoting reaction could not be found.

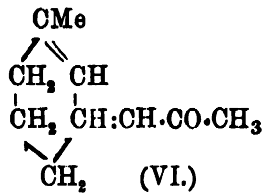
It appears from the experiments carried out that the reactivity of the differently substituted butadiene esters towards sodioesters varies widely, but, on the other hand, slight changes in the experimental conditions have many times been found to have a profound effect in facilitating or inhibiting reaction. It is hoped later to furnish values of the $\alpha\beta$, $\alpha\delta$-ratio for a number of substituted butadiene esters, ketones and nitriles, distinguishing between the effect due to alkylation in the different positions of the chain and that (if any) due to modification of the activating group.

Whether or no the value of the $\alpha\beta$, $\alpha\delta$-ratio in a given instance is at all influenced by changes in the addendum (as,

for instance, by alkylation or replacement of $\cdot CO_2Et$ by $\cdot CN$) remains to be shown, but the indications at present are that such changes affect only the ease of reaction. The influence on the $\alpha\beta$, $\alpha\delta$-ratio of cyclisation is also somewhat doubtful. Many $\alpha\beta$- and $\alpha\delta$-addition products readily undergo cyclisation in the presence of the condensing agent and in some instances it is difficult to find experimental conditions under which addition is promoted but intramolecular cyclisation excluded. For instance, from ethyl methyl*cyclo*hexenylidene-cyanoacetate (V) and methyl*cyclo*hexenylideneacetone (VI) only cyclic $\alpha\beta$-addition products have so far



(V.)



(VI.)

been obtainable, but the legitimacy of concluding that the $\alpha\beta$, $\alpha\delta$-relationship which holds under the cyclising conditions employed is also the normal one is uncertain.

In view of the fact that the formation of a 7—10% yield of one of the ester-addition products of methyl sorbate previously escaped detection, although the search for evidence of such formation was the specific object of investigation, it may well be that the $\alpha\delta$-bromination of β-vinylacrylic acid (Farmer and Healy, *loc. cit.*) and of sorbic acid (Auwers and Heyna, *Annalen*, 1923, **434**, 140) is not quite so complete as ozonisation experiments have indicated. The conclusions of Farmer and Healey with respect to the bromination product of the former acid have recently been endorsed by Muskat, Becker, and Lowenstein (*J. Amer. Chem. Soc.*, 1930, **52**, 326), but the detection and the reasonably efficient isolation of ozone fission products are so much the more difficult of accomplishment when working with diolefin dibromides than when working with unsaturated acids (indeed experience with hydrocarbon dibromides and hydrobromides has clearly

shown the danger of relying on ozonisation technique alone) that a supplementary examination of the bromination products of both acids is very desirable.

EXPERIMENTAL

Addition of Methyl Malonate to Methyl Sorbate.—The yield of addition product previously recorded by Farmer and Healey (*loc. cit.*, p. 1064) was considerably improved by modifying slightly the experimental conditions. Methyl malonate (50 g.) was added to a solution of sodium (0·6 g.) in methyl alcohol (6 c.c.·) and a quantity of ether *insufficient to produce a precipitate* usually about 10 c.c.) was added. From the resulting solution, after being heated on a steam-bath for 6 hours, a mixture of unchanged reactants (b. p. 102—110°/20 mm.) and addition product, (b. p. 172—178°/17 mm.) was isolated. Yield of addition product. 80%.

Hydrogenation of the Addition Product.—The addition product, dissolved in aqueous methyl alcohol, absorbed 2 atoms of hydrogen per molecule when shaken therewith in the presence of colloidal palladium for 4 hours. The reduction product, obtained in quantitative yield, was a colourless oil, b. p. 165—170°/14 mm., which yielded a granular sodium salt when boiled with alcoholic sodium hydroxide (excess of the latter was necessary to ensure complete hydrolysis). After the heating had been continued for 4 hours, the sodium salt was filtered off, freed from alcohol, and boiled with 25% hydrochloric acid until decarboxylation was complete (40 hours). The hydrolysis product, isolated with only small loss, was a colourless oily acid which would not solidify. It was distilled and collected in several fractions, of which those of higher boiling point partly or wholly solidified on standing.

The solid material, after being drained and washed with petroleum (recrystallisation operations proved extremely unsatisfactory), melted at 47° and corresponded in properties with the β-methylpimelic acid (m.p. 48—50°) of Einhorn and Ehret (*Annalen*, 1897, **295**, 179) [Found: *M*(dibasic), 174. Calc., 174]. It was readily convertible into β-methyl*cyclo*-

hexanone on heating with lime, and the ketone yielded a semicarbazone, m. p. 191°, identical with that derived from an authentic specimen.

The liquid acid, still containing a proportion of β-methylpimelic acid, could not be induced to solidify. It was therefore converted into its anhydride by boiling with acetic anhydride for 4 hours, after which the unimolecular anhydride of β-propylglutaric acid could be separated from the polymolecular anhydride of β-methylpimelic acid by distillation. The former compound was a colourless oil, b. p. 175°/20 mm., which yielded β-propylglutaric acid, m. p. 52°, on being heated with caustic alkali and then acidified (compare Day and Thorpe, J., 1920, **117**, 1471), and an anilic acid, m. p. 128°, on treatment with aniline (Day and Thorpe, *lloc. cit.*) (Found: C, 67.3; H, 7.5. Calc, for $C_{14}H_{19}O_3N$: C, 67.45. H, 7.6%); the latter compound partly decomposed above 200°/17 mm. and was rapidly converted into β-methyl-*cyclo*hexanone when heated at atmospheric pressure.

The weight of β-propylglutaric anhydride (estimated as the corresponding anilic acid) derivable from a known weight of the hydrolysed reduction product was ascertained. This figure showed the β-propylglutaric acid content of the acid mixture to be about 7%—improbably more than 10%—of the whole

Addition of Esters to Ethyl γ-Methylsorbate.—The γ-methylsorbic ester was obtained from tiglic aldehyde in 50% yield (b. p. 99—100°/ 15 mm.) by the method of Auwers and Heyna (*Annalen*, 1923, **434**, 162). Since ethyl malonate could not be added to this compound under any of the conditions employed, ethyl cyanoacetate was used in its place.

The conjugated ester (22 g.) was added to a mixture prepared by adding ethyl cyanoacetate (33 g.) to a solution of sodium (0·4 g.) in the minimal quantity of absolute alcohol. No ether was added, since such addition at once precipitated the sodiocyanoacetic ester and subsequently inhibited the formation of an addition product. The reaction mixture,

after being heated for 9 hours on a steam-bath, yielded (i unchanged reactants (b. p. below 130°/18 mm.), (ii) an addition product, and (iii) a very small quantity of a dark-coloured viscous liquid. The addition product was a colourless oil, shown subsequently to be a mixture of *ethyl* α-*cyano*-$\beta\gamma$-*di-methyl*-$\Delta\gamma$-*pentene*-$\alpha\varepsilon$-*dicarboxylate* (III) and *ethyl* α-*cyano*-β-iso*butenylglutarate* (IV) (Found: C, 62·8; H, 7·95. $C_{14}H_{21}O_4N$ requires C, 62·9; H, 7·85%). Yield, 18—40%.

Ozonolysis of the Addition Product.—The addition product, dissolved in chloroform, was ozonised for 30 hours. The ozonide, from which the solvent was removed in the usual way, was decomposed by water, the containing vessel being gradually heated to 50° while a stream of carbon dioxide was passed through it. The escaping vapours were conducted into a solution of dimethyl-dihydroresorcinol, which rapidly deposited a bulky precipitate. The precipitate was the acetaldehyde derivative of dimethyldihydroresorcinol, 1:1-dimethyl-4-ethylidene-3 ; 5-*cyclo*hexadione, m. p. 139° (mixed m. p. with an authentic specimen, 139°).

When the evolution of acetaldehyde had ceased, the reaction mixture, which gave an intense purple colour with ferric chloride (to be expected if either formylacetic ester or its polymeride, α-formylglutaconic ester, were present), was boiled on a sand-bath for about 3 hours to decompose the last trace of ozonide. The bulk of the resulting solution was considerably reduced by distilling off water at diminished pressure and the residue was boiled with 25% hydrochloric acid for 12 hours. After cooling, the acid solution was thoroughly extracted, first with ether and then with chloroform. The solvent was removed from the extracts and the united residues were distilled. Two principal fractions were collected, the first, b. p. 120—125°/10 mm., consisting of crude β-methyllævulic acid (compare Bischoff, *Annalen*, 1881, **206**, 331), the second, b. p. 205—210°/10 mm., the solid keto-dilactone of β-acetylglutaric acid (compare Emery, *Annalen*, 1897, **295**, 104).

The former of these was taken up in water at 0° to separate it from the dissolved dilactone and converted into its semicarbazone. When the precautions necessary to the formation of a normal semicarbazone were followed (Blaise, *Compt. rend.*, 1900, **130**, 1718), the product, after twice recrystallising from aqueous alcohol, decomposed at about 182° but melted at 197°, the temperature recorded by Blaise, when heated on the Maquenne block (Found : C, 44·7; H, 7·0. Calc. for $C_7H_{13}O_3N_3$: C, 44·9; H, 6·9%).

The solid keto-dilactone was sparingly soluble in other but readily soluble in chloroform. It crystallised in colourless needles, m. p. 98—99°, from absolute alcohol (Fittig and Roth, *Annalen*, 1900, **314**, 16, give m. p. 99°; Emery, *loc. cit.*, gives m. p. 101—102°). (Found : C, 53·7; H, 5·1. Calc. for $C_7H_8O_4$: C, 53·85; H, 5·1%).

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Imperial College of Science and Technology,
London S. W. 7

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XV-(B)—Muconic and Hydromuconic Acids. Part V. Ester-addition to Ethyl Muconate.

BY ERNEST HAROLD FARMER AND THAKORBHAI NARANJI MEHTA.

It was previously found (Farmer, J., 1922, **121**, 2015; 1923, **123**, 3324) that when alcoholic ethyl sodiomalonate or ethyl sodiocyanoacetate was heated with ethyl muconate a complex mixture of unidentifiable cyclised products was obtained; when, on the other hand, the reactants were kept for several days at room temperature in an ethereal medium (or in an ethereal medium containing only a very small

proportion of alcohol) addition took place without the occurrence of serious cyclisation. Under the latter conditions, however, the addition product had suffered double-bond displacement and a considerable proportion thereof consisted of the substance (II) * instead of the normal $\alpha\beta$-addition product (I). It was pointed out that equilibration of the three forms (I), (III), and (II) had doubtless

$$\underset{\text{(I.)}}{EtO_2C{\cdot}CH{:}CH{\cdot}CHX{\cdot}CH_2{\cdot}CO_2Et} \qquad \underset{\text{(II.)}}{EtO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CX{:}CH{\cdot}CO_2Et}$$

$$\underset{\text{(III.)}}{EtO_2C{\cdot}CH_2{\cdot}CH{:}CX{\cdot}CH_2{\cdot}CO_2Et} \qquad \underset{\text{(IV.)}}{EtO_2C{\cdot}CH_2{\cdot}CHX{\cdot}CHX{\cdot}CH_2{\cdot}CO_2Et}$$

$$X = CH(CO_2Et)_2 \text{ or } CH(CN){\cdot}CO_2Et$$

taken place (I $\rightleftarrows$ III $\rightleftarrows$ II), but no direct evidence of the presence of (I) and (III) was obtained.

Recently, owing to the very numerous ester-additions successfully carried out under "catalytic" conditions *i. e.*, with the employment of only a small proportion of sodium ethoxide (1/5 to 1/10 mol.), it has seemed advisable to re-investigate the addition in order to discover if the normal $\alpha\beta$-addition product (I) is not indeed obtainable and to prepare, if possible, the double-addition product (IV), which has interesting synthetic applications.

By employing as condensing agent a fractional molecular proportion of sodium dissolved in the minimal quantity of alcohol, the cyclising tendency was entirely checked. The product from ethyl muconate and ethyl malonate was the normal addition product (I), since from both of its fission products (obtained by the action of either neutral permanganate or ozone) good yields of oxalic and tricarballylic acids were obtained. The addition product was, however, not quite free from one or both of the compounds (II) and (III),

* Since this substance is an $\alpha\beta$-substituted glutaconic ester, it doubtless existed alongside and in equilibrium with its $\Delta\beta$-(glutaconic) isomeride.

since its ozone fission product gave a colour with ferric chloride; nevertheless no appreciable amount of either of these was present, since none of the β-keto-esters $EtO_2C{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$, $EtO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH(CO_2Et)_2$, and $EtO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$ or their derivatives proved to be isolable.

The normal addition product was easily obtained in good yield, but it could not be induced to combine with a second molecule of the ester-addendum under "catalytic" conditions.

EXPERIMENTAL.

Addition of Ethyl Malonate to Ethyl Muconate.—Ethyl malonate (16 g.) was added to a solution of sodium (0·375 g.) in absolute alcohol (5 c. c.), and the product diluted with dry ether (150 c. c.). Ethyl muconate was then introduced, and the whole refluxed for 5 hours on a water-bath. After cooling, a solution of acetic acid (1 g.) in water (10 c. c.) was added with rapid shaking. The ethereal liquor was thoroughly washed with sodium carbonate solution and with water, dried, and distilled. It yielded *ethyl* Δ^{a}*-butene-*$\alpha\delta$*-dicarboxylate-*γ*-malonate* as a colourless oil which on redistillation boiled at 175—180°/2 mm. (Found: C, 56·9; H, 7·2. $C_{17}H_{26}O_8$ requires C, 57·0; H, 7·2%). Yield, 70%. The constitution of this addition product, which contained a trace of an isomeric ester, followed from the nature of its degradation products (below).

Ozonolysis of the Addition Product.—This was carried out by submitting a chloroform solution of the addition product (10 g.) to a stream of ozonised oxygen until ozone was no longer absorbed. On removal of the solvent from the product a viscous colourless ozonide remained which was not easily decomposed by water except on boiling. The aqueous decomposition product gave a deep colour with ferric chloride, indicating that to some extent double-bond displace-

ment to the $\beta\gamma$- or $\alpha\beta$-position (yielding ethyl Δ^{α} or β-butene-$\alpha\delta$-dicarboxylate-β-malonate) had taken place. The amount of such displacement was, however, very small, since on complete oxidation of the aldehydic material in the ozonolysis product to the carboxylic acid stage by keeping it for 2 days with perhydrol (30 c. c.) (*i. e.*, until it no longer gave a colour with Schiff's reagent), no neutral material—and consequently no appreciable quantity of either of the ketonic esters which should be formed from the respective Δ^{α}- or Δ^{β}-form of the addition product—remained. This was ascertained by making the oxidation liquor alkaline with sodium carbonate and extracting it with ether. The dissolved acidic esters were hydrolysed by heating with alkali and then decarboxylated by refluxing with 25% hydrochloric acid for 20 hours. By extraction with ether first of the acid liquor, and then of the residue left on evaporation of the latter to dryness, a mixture of acids was obtained from which oxalic acid was removed as calcium oxalate. The residual acid after regeneration from the mother-liquor was found to be crude tricarballylic acid. This was most conveniently purified by converting it into the lead salt and regenerating the acid therefrom with hydrogen sulphide. The tricarballylic acid thus obtained in good yield melted at 160° [mixed m. p., 160°; *M* (tribasic), 175·5]. The residues were acidified and re-extracted, but no trace of another acid was obtained.

Oxidation of the Addition Product with Permanganate.—To the addition product (9·7 g.), dissolved in acetone and cooled to 0°, 3% permanganate solution (containing excess of magnesium sulphate) was gradually added with mechanical stirring. Reduction of permanganate was very rapid until the equivalent of 4 atoms of oxygen per molecule of the addition product (*i. e.*, 500 c. c.) had been added. At this stage reduction ceased and the product was freed from manganese mud in the usual way. The aqueous liquor was evaporated

to dryness, and the residue acidified and extracted with ether. The oil so obtained was hydrolysed with alkali, and afterwards decarboxylated by boiling with 25% hydrochloric acid for 24 hours. The acid liquor was evaporated to dryness and the residue extracted thoroughly with acetone. A viscous liquid was obtained which soon solidified; this was a mixture of oxalic and tricarballylic acids, from which the individual acids were economically separated in fairly good yield by the method described above.

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Imperial College of Science and Technology,
London S. W. 7.

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XV-(C)—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XI. Decomposition of Quaternary Ammonium Hydroxides containing the *tert*-Butylcarbinyl Group.

BY C. K. INGOLD AND C. S. PATEL.

It has been suggested (Part I; J., 1927, 997) that in the decomposition of quaternary ammonium hydroxides having hydrocarbon radicals without a β-hydrogen atom the group which is more stable as a cation will be preferentially eliminated; but the examples given were not conclusive because benzyl, for instance, forms not only a more stable cation than methyl but also a more stable anion. A better comparison would be between methyl and primary alphyl groups, and the suggestion indicated would mean that the ethyl group, $CH_3 \rightarrow CH_2$, should *ceteris paribus* be more readily eliminated than the methyl group, $H—CH_2$, because in the former case the inductive effect represented by the arrow should stabilise the cation. Actually, the issue as between methyl and ethyl is confused by the circumstance that the latter has an alternative mode of elimination, but the *tert.*-

butylcarbinyl group, the simplest primary alphyl group devoid of a β-hydrogen atom, has not this disadvantage, and the argument illustrated for the ethyl group applies with greater force to this higher homologue, $Me_3C \rightarrow CH_2$. We find that the decomposition of *tert.*-butylcarbinyltrimethylammonium hydroxide proceeds substantially in a single direction and that the alcohol eliminated is methyl alcohol. Thus the order of ease of elimination of the radicals concerned, $CH_3 > CMe_3 \cdot CH_2$, is the reverse of that anticipated, and the circumstance that primary and secondary paraffin alcohols have never been observed to appear during the decompositions of ammonium hydroxides can, we think, despite the complication of olefin-elimination, be accepted as indicating an intrinsically smaller tendency in primary and secondary alphyl groups than in the methyl group to undergo elimination as an alcohol. On the other hand the case of the *tert.*-butyl group (Part I, *loc. cit.*) will serve as a warning against incautious generalisation. The position of the benzyl group relatively to methyl and primary alkyl groups follows from our observation that benzyl-*tert.*-butylcarbinyldimethylammonium hydroxide decomposes to the extent of at least 90% in the direction leading to benzyl alcohol and the complementary amine, thus indicating the order,

$$C_6H_5 \cdot CH_2 > H \cdot CH_2 > CMe_3 \cdot CH_2.$$

EXPERIMENTAL.

Preparation.—The most convenient route to *tert.*-butylcarbinylamine and its methyl derivatives was found to be that which proceeds *via* pivalonitrile. Pivalic acid ("Organic Syntheses," VIII, 108) was converted into its chloride, b. p. 103° (Butlerow, *Annalen*, 1874, **173**, 373, who used PCl_5, records 105—106°), by treatment on the water-bath with $SOCl_2$, and thence into the amide, m. p. 155°, by means of well-cooled conc. ac. NH_3 and crystn. from H_2O to remove NH_4Cl. From the amide, the nitrile, m.p. 15°, b. p, 106°, was prepared

(Butlerow, *loc. cit.*), and this was reduced (Freund and Lenze, *Ber.*, 1890, **23**, 2867; 1891, **24**, 2156; Tissier, *Ann. Chim. Phys.*, 1893, **29**, 373) to the primary amine, b. p. 80—82°, of which the hydrochloride had m.p. 274° (decomp.), the *picrate*, leaflets from alcohol, m. p. 205° (Found: C, 41.9; H, 5.15. $C_{11}H_{16}$-O_7N_4 requires C, 41.8; H, 5.06%), and the acetyl derivative, m.p. 75°. Methylation of the primary amine to the tertiary stage was accomplished by Eschweiler's general method (*Ber.*, 1905, **38**, 881), a mixture of the hydrochloride (10 g.) and paraformaldehyde being heated under reflux at 140° (bath temp.) for 3 hr. Treatment with conc. aq. KOH gave an oil consisting of tert. *butylcarbinyldimethylamine*, which after drying with KOH and with Na had b. p. 96—97° (Found: C, 72.9; H, 14.6. $C_7H_{17}N$ requires C, 73.0; H, 14.8%). The *hydrochloride*, prepared in Et_2O-EtOH and cryst. from EtOH, formed hygroscopic prismatic plates, m. p. 182° (Found: Cl, 23.15. $C_7H_{17}N$,-HCl requires Cl, 23.4%), the *hydrobromide* was obtained as hygroscopic needles, m. p. 170° (Found: Br, 40.8. $C_7H_{17}N$, HBr requires Br, 40.8%) and the *hydriodide* as small crystals, m. p. 135° (Found: I 52.8. $C_7H_{17}N$,HI requires I, 52.3%). The *picrate*, pptd. from Et_2O and cryst. from EtOH, formed stout needles, m. p. 193° (Found: C, 45.6; H, 5.9. C_{13} $H_{20}O_7N_4$ requires C, 45.3; H, 5.8%). A mixture of the tertiary base (5 g.) and MeI (7 g.) was kept for 4 hr, at room temp. and the solid mass formed was ground with Et_2O and crystallised from EtOH, tert.-*butylcarbinyltrimethylammonium iodide* (10 g.) being obtained as a microcryst. mass, m. p. 240° (decomp.) (Found: I, 49.1. $C_8H_{20}NI$ requires I, 49.4%). Similarly the *tert.*-amine (7 g.) and benzyl bromide (12 g.) yielded *benzyl*-tert.-*butylcarbinyldimethylammonium bromide*, which, similarly purified, had m. p. 200° (decomp.) (Found: Br, 27.7. $C_{14}H_{24}NBr$ requires Br, 28.0%).

tert.-Butylcarbinyldimethylamine was also obtained, though in small yield, by the action of *tert*—butylmagnesium chloride on dimethylaminomethyl *n*-butyl ether (McLeod and Robinson, J., 1921, **119**, 1470).

tert.-Butylcarbinol, prepared by reduction of ethyl pivalate (Richards, *Ann. Chim. Phys.*, 1910, **21**, 337), was converted into the iodide with red P and I, Tissier's method (*loc. cit.*) being unsuccessful in our hands. On treatment with dimethylamine this iodide yielded the hydriodide of the original amine (cf. Noller and Dinsmore, *J. Amer. Chem. Soc.*, 1931, **53**, 1185; 1932, **54**, 1025).

Decomposition of Hydroxides.—A solution of *tert.*-butylcarbinyltrimethylammonium hydroxide was prepared from the iodide (11·9 g.) and a small excess of Ag_2O. Preliminary expts. having shown that the decomp. of the hydroxide yielded no gaseous products (substances which could be collected in dil. acid or Br after condensation of the aq. distillate), the hydroxide solution was distilled (bath temp. 150—200°) in the ordinary way. The distillate yielded 4·95 g. of pure *tert.*-butylcarbinyldimethylamine and the basic residues, when worked up as hydrochlorides, gave 0·82 g. of the salt of the same amine (total yield, 93%). The small loss appeared to be mainly mechanical, a careful search failing to reveal the presence of *tert.*-butylcarbinol or trimethylamine. MeOH was found in quantity and identified as methyl *p*-nitrobenzoate.

The decomposition of benzyl-*tert.*-butylcarbinyldimethylammonium hydroxide was conducted in the same way, and pure *tert.*-butylcarbinyldimethylamine was isolated in 90% yield. Benzyl alcohol was isolated in quantity, but neither MeOH nor *tert.*-butylcarbinol could be obtained.

University of Leeds.
University College, London.

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XVI. A Study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene Group.

Part I. The Formation of Sulphoxides.

BY K. G. NAIK, R. D. DESAI AND M. M. PAREKH.

During the investigations of the reaction between sulphuryl chloride and substances containing the reactive methylene ($—CH_2—$) group, it was observed that sulphuryl chloride invariably acts as a chlorinating agent (Naik and Shah, *J. Indian Chem. Soc.*, 1927, **4**, 11). It was therefore, thought interesting to investigate the action of thionyl chloride on these substances, specially as it reacts with other compounds, giving rise to various products depending upon the conditions of the experiments.

The reactions of thionyl chloride may be roughly divided under three different heads. It reacts as—

(*i*) A chlorinating agent replacing groups such as (*a*)—OH, (*b*) —SH, (*c*) $—NO_2$, (*d*) $—SO_3H$, and (*e*) —H by chlorine (Meyer, *Monatsh.*, 1901, **22**, 415; D. R. P. 201325.6, Frankland and Garner, *J. Chem. Soc.* 1914, **105**, 1101; Barbier anh Locquin, *Bull. Soc. Chim.*, 1912, **11**, 223; Stähler and Schirm *Ber.*, 1911, **44**, 319; McKenzie and Clough, *J. Chem. Soc.*, 1913, **103**, 687; Barger and Ewins, *ibid*, 1908, **93**, 735; Silberrad, *ibid*, 1921, **119**, 2029; Meyer, *Monatsh.*, 1915, **36**, 723; Pollak and Rudich, *ibid*, 1922, **43**, 2029; Majima and Simanuki, *Proc. Imp. Acad. Tokyo*, 1926, **2**, 544).

(*ii*) A dehydrating agent (Denham and Woodhouse, *J. Chem. Soc.*, 1913, **103**, 1861; Michaelis and Sieber, *Annalen*, 1893, **274**, 312; Meyer, *Monatsh.*, 1902, **23**, 897; Lasch, *Monatsh.*, 1913, **34**, 1653; Pawlewski, *Bull. Acad. Sci. Cracow*, 1903, 8; Wohl, *Ber.*, 1909, **40**, 4698).

(*iii*) A "thionating" agent giving rise to sulphonium chlorides, sulphoxides and sulphides (Colby and McLoughlin *Ber.*, 1887, **20**, 195; Parker, *Ber.*, 1890, **23**, 1844; Smiles and

Bain, *J. Chem. Soc.*, 1907, **91**, 1718; Gazdar and Smiles, *J. Chem. Soc.*, 1910, **97**, 2249; Smiles and Le Rossignol, *J. Chem. Soc.*, 1906, **89**, 697; 1908, **93**, 745; Michaelis and collaborators, *Ber.*, 1890, **23**, 3480; 1891, **24**, 745; 1893, **26**, 2158; 1897, **30**, 1009; *Annalen*, 1893, **274**, 173, 187, 200; Francke, *Ber.*, 1898, **31**, 2178; Rosenheim and Sarow, *Ber.*, 1905, **38**, 1298; Green, *J. Chem. Soc.*, 1924 **125**, 1450).

It is thus evident from the literature that thionyl chloride will react in a very interesting manner, as it does with phenols and amines with which the reactive methylene ($—CH_2—$) group has many points of similarity in reaction. With these ideas in view, the reaction of thionyl chloride was studied first on malon-diphenylamide in presence of dry benzene. A vigorous evolution of hydrochloric acid gas took place, changing the colour of the solution to red, which gave yellowish-red needles. The course of the reaction may be given as follows:—

$$(RNH{\cdot}CO)_2CH_2 + SOCl_2 = (RNH{\cdot}CO)_2C : SO + 2HCl$$

(where R = phenyl, tolyl, xylyl or *a*-naphthyl groups or one of the R is a hydrogen.)

The above constitution of the compound follows from the following considerations :—

(i) That the two hydrogen atoms are not supplied by the phenyl group, because—

(*a*) Malon-dimethylamide, which possesses no such phenyl group, gives the compound $SO : [CH(CO{\cdot}NHCH_3)_2]_2$.

(*b*) Malon-monophenylamide which possesses only one phenyl group, gives the compound, malon-monophenylamide sulphoxide. If the phenyl group be reactive such a compound cannot be expected.

(*c*) The sulphoxides obtained are very unstable whereas those having the grouping –SO– in the nucleus are very stable (Colby and McLoughlin, Parker, *loc. cit.*).

(ii) That the hydrogen atoms eliminated are not those that are attached to the nitrogen atom of the –NHR group, because

(*a*) Malon-dimethylphenylamide, with contains no such amidohydrogen, reacts with thionyl chloride.

(*b*) Only one hydrogen is replaced in malon-dimethylamide, though it contains two such amido-hydrogens.

Thionyl chloride was made to react with the following amides :—

(1) Malon-diphenylamide, (2) malon-di-*o*-tolylamide, (3) malon-di-*m*-tolylamide, (4) malon-di-*p*-tolylamide, (5) malon-di-(1 : 4 : 5)xylidide, (6) malon-di-*a*-naphthylamide, (7) malon-di-*β*-naphthylamide, (8) malon-mono-phenylamide, (9) malon-mono-*o*-tolylamide, (10) malon-mono-*m*-tolylamide, (11) malon-mono-*p*-tolylamide, (12) malon-mono-*a*-naphthylamide, (13) malon-mono-*β*-naphthylamide, (14) malon-di-methylphenylamide, (15) malon-*p*-tolylamate. (16) malon-*o*-tolylamate, (17) malon-dimethylamide, (18) malon-diethylamide, (19) malon-dipropylamide, (20) and (21) malon-dibutylamide (*n* and *iso*-), (22) malonamide, and the amides of methylmalonic acid.

Of the above, (1) to (16) reacted to give sulphoxides

$$(RNH{\cdot}CO)_2CH_2 + SOCl_2 = (RNH.CO)_2C : SO + 2HCl;$$

but in the case of amides (14), (15) and (16) the reaction products were liquids, which did not solidify even when kept in a freezing mixture. Hence they were not worked up for the present.

In the case of (17) and (18) only one hydrogen atom of the methylene group was found to be reactive, the reaction taking the following course :

$$2(CH_3NH.CO_2)CH_2 + SOCl_2 = [(CH_3NH{\cdot}CO)_2CH]_2{:}SO + 2HCl.$$

This type of reaction is not unusual. Many instances may be cited in which only one hydrogen atom of the methylene group had become reactive. Sulphur monochloride reacted with malondimethylphenylamide giving a disulphide (Ph (Me)N· CO)$_2$CH]$_2$S$_2$ (Naik, J. Chem. Soc., 1921, **119**, 379; a monochloro-derivative of the same was obtained by West (J. Chem. Soc., 1922, **121**, 2196) by the action of free chlorine

and by Naik and Shah (loc. cit.) by sulphuryl chloride on the same substance. Malon-dipropylamide monosulphonic acid was obtained by the action of chlorosulphonic acid on malon-dipropylamide (Naik and Shah, under publication). Such a type of reaction has generally been explained by supposing that the second hydrogen atom became sluggish after the first was replaced by the substituent. In the case of (22) no reaction takes place under the conditions generally observed in these experiments. In the case of all the remaining amides a vigorous evolution of hydrogen chloride was observed but no definite reaction product could be separated because in all probability the sulphoxides formed were decomposed during the precipitation, owing to the unstable nature of such compounds.

From the above results it can be seen that in a series like:— (i) $CH_2(CO{\cdot}NH_2)_2$, (ii) $CH_2(CO{\cdot}NHCH_3)_2$, (iii) $NH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NHR$, (iv) $CH_2(CO{\cdot}NHR)_2$, (v) $CO_2C_2H_5{\cdot}CH_2{\cdot}CO{\cdot}NHR$ the reactivity of the hydrogen atoms of the methylene group, which is absent in (i), starts in (ii) and goes on increasing. This can be explained as the effect of the increase of the negative character of the two carbonyl groups adjacent to the reactive methylene group in all the compounds; for malonamide, in which the two amino–groups completely neutralise the negative character of the carbonyl groups attached to the methylene group, does not react with thionyl chloride, whereas, in all the other cases, the basic character of the other substituted amino-groupings attached to the carbonyl group being progressively reduced, the hydrogen atoms of the reactive methylene group are thrown into reactivity with increasing vigour. This reactivity is seen enhanced, when one or both of the amino-groups are replaced by negative groups, like phenyl, tolyl, naphthyl. etc. In the case of (v) where one of the amino groups in completely replaced by a carbethoxy group, the reaction is exceptionally vigorous.

Three different hypotheses are put forth to explain the course of the reactivity depending upon the total negativity, name-

ly, (1) polarity hypothesis (Macbeth and collaborators, *J. Chem. Soc.* 1922, **121**, 892, 904, 1109, 2169, 2527, 2601; 1923 **123**, 1121, 1925; 1925, **127**, 892, 1118; (2) keto-enol transformation Thorpe and collaborators, *J.* Chem Soc, 1911, **99**, 2183 1921, **119**, 1 03; 1922, **121**, 1896; (3) the combined effect of polarity and steric hindrances as would give rise to keto-enol transformations (West, *J. Chem. Soc.*, 1924, **125**. 710). The course of the reaction in the case of the compounds investigated can be represented on the keto-enol hypothesis. Taking the case of malon-diphenylamide (according to Norris and Thorpe.)

$$PhNH\cdot CO\cdot CH_2\,CO\,NHPh \longrightarrow PhNH.CO\cdot CH{:}C(OH)\cdot NHPh$$

$$\xrightarrow{SOCl_2} \underset{\text{(unstable)}}{PhNH\cdot CO\cdot CH : \underset{SOCl}{\underset{|}{C}}O\cdot NHPh} \longrightarrow PhNH\cdot CO\cdot \underset{SOCl}{\underset{|}{C}}H\cdot NHPh$$

The second hydrogen atom will again tautomerise and will remove the second chlorine atom, giving rise to $(C_6H_5NH\cdot CO)_2$ C:SO. In the case of substances, where the second hydrogen atom remains sluggish, the second chlorine atom is removed by the other molecule.

It is interesting to observe that these sulphoxides give rise to sulphides, when heated with dry benzene in presence of a dry catalyst such as hydrochloric acid gas and iodine. This will form the subject of a future communication.

EXPERIMENTAL.

Malon-diphenylamide sulphoxide.—Two g. of malon- diphenylamide were made to interact with 1·6 g. of thionyl chloride in presence of 25 c. c. of dry benzene, on a water-bath. After an hour and a half, when the evolution of hydrochloric acid had nearly ceased, the mixture was concentrated and the compound was precipitated by slow addition of dry petroleum (b. p. 50-60°). It came out in the form of yellowish-red needles. It was washed free from thionyl chloride by dry petroleum. It melted with decomposition at 129°. It is easily decomposed by water and alcohol giving the original amide and sulphur dioxide. (Found: S, 10-56; N, 9·52. $C_{15}H_{12}N_2O_3S$ requires S, 10·66; N. 9·32 per cent.).

Malon-di-o-iolylamide sulphoxide.—Three g. of the amide were allowed to react with 1·6 g. of thionyl chloride as above. It gave a deep red crystalline compound, melting at 129-30°. It is easily decomposed by water and alcohol. (Found: S, 9 61, $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.)

Malon-di-m-tolylamide sulphoxide.—It was prepared from 3 g. of the amide and 1·6 g. of thionyl chloride. It was a saffron coloured crystalline compound, which melted at 142-43°. It is decomposed by water and alcohol. (Found: S, 9·87. $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.).

Malon-di-p-tolylamide sulphoxide.—It was prepared like the above compound. It is a deep red crystalline compound. It decomposes above 170° and melts at 215°, It is decomposed by water and alcohol. (Found:S, 9·65. $C_{17}H_{16}O_3N_2S$ requires S, 9·75 per cent.).

Malon-di-α-naphthylamide.—It was similarly prepared from 3·4 g. of the amide and 1·6 gr of thionyl chloride. It came out in the form of charcoal-black needles. It decomposes at 165° and melts at 210°. It is decomposed by water and alcohol. (Found: S, 8·22. $C_{23}H_{16}O_3N_2S$ requires S, 8·00 per cent.)

Malon-di-β-naphthylamide sulphoxide.—It was prepared like the previous compound. They are deep red needle-shaped crystals. These decompose above 170°. and melt at 166°. It is decomposed by water and alcohol. (Found : S, 8·23. $C_{23}H_{16}O_3N_2S$ requires S, 8·00 percent.).

Malon-di(1: 4: 5:)-xylidide sulphoxide.—It was prepared from 3·1 g. of the amide and 1·6 g. of thionyl chloride. It gave deep red needles. They melt at 172-3°. It is decomposed by water and alcohol. (Found: S, 9·06. $C_{19}H_{20}O_3N_2S$ requires S, 8·96 per cent.).

Malonmonophenylamide sulphoxide.—It was prepared from 2 g. of the amide and 1·4 g. of thionyl chloride. Yellowish-red needles were obtained. The product melts at 150°. It is decomposed by water and alcohol. (Found : S, 14·54. $C_9H_8O_3N_2S$ requires S, 14·28 per cent.).

Malon-mono-p-tolylamide sulphoxide.— It was prepared from 2·1 g. of the amide and 1·4 g. of thionyl chloride. It came down in the form of chocolate coloured needles, m. p. 156-7°. It is decomposed by water and alcohol. (Found: S, 13·46. $C_{10}H_{10}O_3N_2S$ requires S, 13·44 per cent.).

Preparation of Malon-mono-m-tolylamide.—Ethyl malonate (25 g.) and *m*-toluidine (11 g.) were mixed in a round-bottomed flask, having a wide upright tube passing through the cork, fitted in the mouth of the flask. The length of the tube from the cork upwards to the bent, measured 15 cms, the flask was heated in a paraffin–bath maintained at a temperature of 120-125°. The rate at which the alcohol was allowed to distill was regulated in such a way that the ester got no chance of being distilled out. After heating for eight hours, the contents were transferred to a stoppered bottle and were mixed with twice its amount of ammonia (*d* 0·88) This was shaken for four hours. The semi-solid mass was transferred to a beaker and evaporated till it was nearly solid. This mass which was a mixture of malon-di-*m*-tolylamide, malon-mono-*m*-tolylamide and malonamide, was filtered at the pump after cooling and washed with ether to remove the unreacted amine. It was boiled with alcohol and water (1 : 6) and filtered hot. This kept the insoluble diamide on the filter paper. The liquid deposited white thick needles on cooling the malonamide being kept in solution. The product melts at 165°. It is very soluble in hot water, methyl and ethyl alcohol, acetic acid, and sparingly so in cold water, hot benzene and hot carbon tetrachloride. It is insoluble in petroleum. (Found: N, 14·46. $C_{10}H_{12}O_2N_2$ requires N, 14·58 per cent.).

Malo-mono-m-tolylamide sulphoxide :—It was prepared like the previous sulphoxide. It gave yellowish-red needles, m.p. 140°. It is decomposed by water and alcohol. (Found : S, 13·45. $C_{10}H_{10}O_3N_2S$ requires S. 13·44 per cent.)

Malon-mono-o tolylamide :—Ethyl malonate (25 g.) and *o*-toluidine (11 g.) were heated under the same conditions as

stated above, and treated likewise. It gave thick white needles, m. p. 162°. It is soluble in cold water, hot benzene and carbon tetrachloride, and insoluble in petroleum. (Found : S, 15·04. $C_{10}H_{12}N_2O_2$ requires N, 15·58 per cent.

Malon-mono-o-tolylamide sulphoxide:—It was prepared from 2·1 g. of the amide and 1·4 g. of thionyl chloride. It formed deep red crystals, m. p. 168°. The product is decomposed by water and alcohol. (Found : S, 13·58. $C_{10}H_{10}O_3N_2S$ requires S, 13·44 per cent).

Malon-mono-a-naphthylamide :—Ethyl malonate (25 g.) and α-naphthylamine (14·1 g.) were condensed under identical conditions. After the usual treatment, it gave reddish needles, which after recrystallisation melted at 146°. It is very soluble in hot water, methyl and ethyl alcohol and acetic acid, and sparingly so in cold water, hot benzene and carbon tetrachloride. It is insoluble in petroleum. (Found : N, 11·96. $C_{13}H_{12}O_2N_2$ requires N, 12·28 per cent.).

Malon-mono-a-naphthylamide sulphoxide :—It was prepared from 2·5 g. of the amide and 1·4 g. of thionyl chloride. It forms deeply coloured needles, melting at 170°. It is decomposed by water and alcohol. (Found : S, 11·92. $C_{13}H_{10}O_3N_2S$ requires S, 11·64 per cent.).

Malon-mono-β-naphthylamide :—Ethyl malonate (25 g.) and β-naphthylamine (14·1 g.) were similarly condensed and treated. The eqeous-alcoholic solution gave white leaflets, m. p. 188°. In solubility it resembles the previous amide. (Found : N, 12·32. $C_{13}H_{12}O_2N_2$ requires N, 12·28 per cent.)

Malon-mono-β-naphthylamide sulphoxide:—It was prepared like the last sulphoxide. It forms chocolate coloured needles, m. p. 160°. It is decomposed by water and alcohol. (Found : S, 11·87. $C_{13}H_{10}O_3N_2S$ requires S, 11·64 per cent.).

Bis-malon-dimethylamide sulphoxide:—Two g. of malon-dimethylamide sulphoxide were made to react with 1·8 g. of thionyl chloride in 25 c .c. of dry benzene. After half an hour a white crystalline substance separated. When the evolution

of hydrogen chloride had ceased, the reaction product was separated and filtered and washed with dry petroleum. It melts at 208°. It is sparingly soluble in benzene, but insoluble in toluene and petroleum. It is not decomposed by alcohol but is slowly decomposed by hot alcohol. (Found : S, 10·01, $C_{10}H_{18}O_5N_4S$ requires S, 10·45 per cent.).

Bis-malon-dimethylamide sulphoxide :—It was similarly obtained. It melts at 176°. The product is sparingly soluble in benzene and insoluble in toluene and petroleum. It is not decomposed by cold alcohol and water. (Found : S, 8·64. $C_{14}H_{26}O_5N_4S$ requires S, 8.81 per cent).

The authors take this opportunity to express their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (M.M.P.) wishes to record his gratitude to His Highness the Maharaja of Bhavanagar for granting a scholarship, which enabled him to carry out the research.

CHEMISTRY DEPARTMENT,
BARODA COLLEGE,-BARODA.

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XVII. A Study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene Group. Part II. Conversion of Sulphoxides into Sulphides.

BY: K. G. NAIK AND M. M. PAREKH.

While studying the action of thionyl chloride on malon-diphenyl amide, it was found that if the reaction mixture was heated for more than four hours, a yellowish-white crystalline substance was precipitated. This compound was found to have the constitution, $(C_6H_5NH{\cdot}CO)_2\ C{:}S{:}C(CO{\cdot}NHC_6H_5)_2$(I)

This behaviour of malon-diphenylamide is not surprising in view of the fact that thionyl chloride does react with

different substances, giving rise to different products, depending on the conditions of the experiment (Michaelis and Philips, *Ber.*, 1890, **23**, 559; Sprauge, *J Chem Soc.*, 1891, **59**, 321; Jassinarri, *Gazzetta*, 1890, **20**, 362; Voswinkel, *Pharm.Z.*, 1895, **40**, 241; Loth and Michaelis, *Ber.*, 1894, **27**, 2540; Michaelis and Godchaux, *Ber*; 1890, **23**, 553; Michaelis and Schindlar, *Annalen* 1899, **310** 137).

A sulphide similar to the above was also obtained by Michaelis and Philips (*loc cit.*) by the interaction of thionyl chloride and aceto-acetic ester, to which they attributed the constitution (II).

The course of the reaction was explained by them on the assumption that thionyl chloride decomposes into sulphur dichloride and sulphuryl chloride; and the sulphur dichloride thus formed reacts with the ester as under:—

$$2SOCl_2 = SCl_2 + SO_2Cl_2 \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$2\ \begin{matrix} CH_3CO \\ CO_2Et \end{matrix}\!\!>\!CH_2 + SCl_2 = \left[\begin{matrix} CH_3CO \\ CO_2Et \end{matrix}\!\!>\!CH\right]_2 S + 2HCl \ldots(2)$$

(11)

Michaelis and Loth observed that thionyl chloride reacted as under, with phenols, the final products of the reaction being sulphides:

$$2C_6H_5{\cdot}OH + SOCl_2 = (OH{\cdot}C_6H_4)_2SO + 2HCl \ldots\ldots\ldots(3)$$

A

$$(OH.C_6H_4)_2SO + SOCl_2 = (OH{\cdot}C_6H_4)_2S + SO_2 + Cl_2 \ldots\ldots(4)$$

B

Here the formation of sulphides from sulphoxides was attributed by them to "the reducing action of thionyl chloride." This was supported by the fact that the substance (B), on treatment with nitric acid, gave the substance (A).

It must however, be pointed out that the formation of the sulphides from sulphoxides, as observed here, cannot be explained on any of the above hypotheses. The hypothesis of Michaelis and Philips presupposes the assumption that thionyl

chloride decomposes into sulphur dichloride and sulphuryl chloride. The reaction of sulphur dichloride with substances containing the reactive methylene group has already been studied in this laboratory by Naik and Jadhav (*J. Indian Chem. Soc*; 1926, **3**, 261), and in no case was a sulphide of the type represented by Michealis and Philips obtained, the compounds formed having the constitution—

$$\begin{array}{l}\mathrm{R{\cdot}CO}\\ \mathrm{R{\cdot}CO}\end{array}\!\!>\!C\!<\!\!\begin{array}{l}\mathrm{SCl}\\ \mathrm{SCl}\end{array} \qquad \text{or} \qquad \begin{array}{l}\mathrm{R{\cdot}CO}\\ \mathrm{R{\cdot}CO}\end{array}\!\!>\!\mathrm{CH\,SCl}$$

(C) (D)

Again Naik and Shah (*J. Indian Chem, Soc.*, 1927, **4**,11) have observed during the investigation of the action of sulphuryl chloride on the same substances, that chloro-compounds of the type,

$$\begin{array}{l}\mathrm{—CO}\\ \mathrm{—CO}\end{array}\!\!>\!C\!<\!\!\begin{array}{l}\mathrm{Cl}\\ \mathrm{Cl}\end{array} \qquad \text{or} \qquad \begin{array}{l}\mathrm{—CO}\\ \mathrm{—OO}\end{array}\!\!>\!\mathrm{CH{\cdot}Cl}$$

(E) (F)

are formed. Finally the chlorine disengaged as per (4) above would produce chloro-compounds similar to the above (*cf.* West *J. Chem Soc.*, 1924, **125**, 100). Had the course of the reaction been as represented by Michaelis and Philips or Michaelis and Loth, compounds of the type (C), (D), (E), or (F) should have been obtained, whereas during the present work no such compounds were isolated.

Further, if the reaction proceeded as represented by Michaelis and Loth, the resulting sulphide would possess the constitution (G), thus:

$$\begin{array}{l}\mathrm{—CO}\\ \mathrm{—CO}\end{array}\!\!>\!\mathrm{C:SO}+\mathrm{SOCl_2} \rightarrow \begin{array}{l}\mathrm{—CO}\\ \mathrm{—CO}\end{array}\!\!>\!\mathrm{C:S}+\mathrm{SO_2}+\mathrm{Cl_2}$$

(G)

whereas the sulphides obtained here have the constitution.

$$\mathrm{(RNH{\cdot}CO)_2C{:}S{:}C(CO{\cdot}NHR)_2}$$

That the sulphides have the constitutions assigned to them as above follows from the fact that, thio-bis-malon-diphenylamide when hydrolysed with caustic alkali yields aniline as one of the products of hydrolysis. From this it is clear that the sulphur is neither attached to the nitrogen nor to any of the carbon atoms in the nucleus.

From the above considerations, one is led to suggest that the course of the reaction in the present case is entirely different from that represented by Michaelis and Philips or Michaelis and Loth. The formation of the sulphides from the sulphoxides can be well explained in the following manner :—

$$(RNH{\cdot}CO)_2C{:}S{:}O + O{:}S{:}C(CO{\cdot}NHR)_2 = [(RNH{\cdot}CO)_2C]_2 : S + SO_2$$
$$\text{(H)}$$

where R may be a tolyl, a phenyl or a naphthyl grouping.

This reaction may proceed either (*i*) spontaneously or (*ii*) in the presence of a catalyst (here thionyl chloride acts as the catalyst). In order to decide this point freshly prepared malon-diphenylamide sulphoxide was heated in dry benzene solution (*a*) alone, (*b*) in the presence of thionyl chloride, (*c*) in the presence of dry hydrochloric acid gas, and (*d*) in the presence of iodine. In experiment (*a*) the original malon-diphenylamide was obtained back; whereas in all the other cases a distinct steady evolution of sulphur dioxide was preceived and the sulphide was isolated as the final product. This definitely points to the conclusion that the sulphides are formed from the sulphoxides under the influence of the catalysts such as, thionyl chloride, hydrochloric acid gas or iodine.

The investigation in connection with the formation of sulphides from sulphoxides was carried out in the case of the sulphoxides obtained from the following amides :—

(1) Malon-diphenylamide, (2) malon-di-*o*-tolylmide, (3) malon-di-*m*-tolylamide, (4) malon-di-*p*-tolylmide, (5) malon-di-*α*-naphthylamide, (6) malon-di-*β*-naphthylamide, (7) malon-monophenylamide, and (8) malon-mono-*m*-tolylamide.

In all the cases sulphides similar to (H) were obtained; except in (5) and (6), where besides these sulphides, by-pro-

ducts not containing sulphur and having melting points higher than those of the original amides were obtained. These are still under investigation.

EXPERIMENTAL.

Thio-bis-malon-diphenylamide (1).—Malon-diphenylamide (1·2 g.) was heated with thionyl chloride (0.9 g.) for four hours, after which a solid began to separate. The reaction was continued till there was no further separation of the solid. The compound was filtered after cooling, and washed with dry petroleum (b. p. 53°). It was then boiled with dry petroleum to remove the adhering colour and crystallised from alcohol; m.p. 196°. It is fairly soluble in benzene, alcohol and acetic acid, but insoluble in petroleum and water. (Found : S 6·07; N, 10·62. $C_{30}H_{24}N_4O_4S$ requires S, 5·96 ; N, 10·44 per cent).

Action of dry Hydrochloric Acid on Malon-diphenylamide Sulphoxide :—One g. of freshly prepared sulphoxide was dissolved in 25 c. c. of dry benzene and heated under reflux. Dry hydrochloric acid gas was then slowly passed through this solution. After some time a solid began to separate. The reaction was carried on till there was no evolution of sulphur dioxide. It was filtered and washed with petroleum; it was found to be identical with (1) obtained above.

Action of Iodine :—The above sulphoxide (1 g.) was dissolved in 25 c. c. of dry benzene and 0·4 g. of iodine was added to it. The mixture was heated under reflux for about half an hour, when a solid began to separate. When the evolution of sulphur dioxide had ceased, the compound was filtered and washed with alcohol. It was crystallised from alcohol and subsequently found to be identical with the thio-bis-malon-diphenylamide, obtained in the last two cases.

Hydrolysis of Thio-bis malon-diphenylamide :—The thio-compound (3 g.) was refluxed with caustic potash (7 g.) dissolved in 10 c.c. of water for two hours. A heavy liquid separated out; the mixture was extracted with ether, which on evaporation left a liquid, which was identified as aniline. The

aqueous solution was evaporated on a water-bath when a solid was obtained, which on treatment with hydrochloric acid evolved hydrogen sulphide. In all probability the " thio ". grouping was deccomposed during the hydrolysis giving rise to potassium sulphide, which evolved hydrogen sulphide.

Thio-bis malon-di-o-tolylamide.—It was similarly prepared from 1·5 g. of the amide and 0·9 g. of thionyl chloride by heating for four hours. The compound was crystallised from alcohol in white needles, m. p. 214°. It is soluble in alcohol and acetic acid but insoluble in petroleum and water. (Found: S, 5·07. $C_{34}H_{32}O_4N_4S$ requires S, 5·41 per cent.).

Thio-bi-malon di-m-tolylamide.—It was prepared like the previous compound. The substance was precipitated by slowly adding the solution to a large amount of petroleum. This was repeatedly done by dissolving the compound in benzene and reprecipitating with petroleum till the melting point was constant. It is a dirty yellow substance, m. p. 164°. It is soluble in benzene and acetic acid but insoluble in petroleum. (Found:S, 5·45. $C_{34}H_{32}O_4N_4S$ requires S, 5.41 per cent.).

Thio-bis-malon-di-p-tolylamide.—It was prepared as usual. The precipitated substance was filtered and washed with petroleum, and then boiled with alcohol to remove the adhering colour. It is a deep yellow substance and melts at 198°. It is very soluble in acetic acid and sparingly soluble in benzene and alcohol, but insoluble in petroleum. Found: S, 5·71. $C_{34}H_{32}O_4N_4S$ requires S, 5·41 per cent.),

Thio-bis-malon-di-a-naphthylamide.—Malon-di-*a*-naphthylamide (1·7 g.) was refluxed in benzene with 0·9 g. of thionyl chloride, for four hours. A substance was precipitated, which was filtered. On examination it was found to contain no sulphur (m. p. 248°). The filtrate was then added to a large amount of petroleum, when a compound was precipitated. After repeated reprecipitations, it was found to melt at 132°. It is very soluble in benzene and acetic acid but insoluble in petroleum. (Found: S, 4·04. $C_{46}H_{32}O_4N_4S$ requires S, 4·34 per cent.).

Thio-bis-malon-di-β-naphthylamide.—This was prepared likethe previous compound. The substance precipitated during heating contained no sulphut and melted at 265°. The "thio" compound was precipitated from the solution by petroleum. After purification it melts at 146°. It is a dirty yellow substance soluble in benzene and acetic acid but insoluble in petroleum. Found:S, 4·66. $C_{46}H_{32}O_4N_4S$ requires S, 4·34 per cent.).

Thio-bis-malon-monophenylamide.—It was prepared like the other thio-compounds. After repeated reprecipitations, it was found to melt at 114°. It is soluble in benzene and acetic acid but insoluble in petroleum. Found: S;8·46. $C_{18}H_{16}O_4N_4S$ requires S, 8·33 per cent.).

Thio-bis-malon-m-tolylamide.—This was prepared as usual. It is a yellow substance, m. p. 123°. It is soluble in benzene and acetic acid but insoluble in petroleum and water. (Found: S, 7·58. $C_{20}H_{20}O_4N_4S$ requires S, 7·77 per cent.).

The authors desire to record their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work. One of the authors (M.M.P.) also desires to express his gratitude to H. H. the Maharaja of Bhavnagar for a scholarship which enabled him to carry on this work.

CHEMISTRY DEPARTMENT,
BARODA COLLEGE, BARODA.

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XVIII. A Study of the Interaction of Selenium TetrachlorideWith Substances Containing the Reactive Methylene Group.

BY K. G. NAIK AND R. K. TRIVEDI.

Interactions of 1:3-diketones with selenium tetrachloride seem to have been studied by various workers.* The subject matter of the present paper consists of a study of the interaction of selenium tetrachloride with the substituted amides of malonic acid. It was undertaken with a view to study the reactivity of the hydrogen atoms of the methylene ($\cdot CH_2 \cdot$) group in amides and substituted amides of malonic acid.

In view of the decomposition of selenium tetrachloride studied by Taylor, Prideaux and Pool (*J. Amer. Chem. Soc.*, 1926, **48**, 2129), it is not improbable that in the present interaction it may decompose as—

$$2Se\,Cl_4 = Se_2 + 3Cl_2,$$

As such, it was expected that in the present interaction, the reactivity of selenium tetrachloride will be similar to that of sulphur monochloride (Naik *J Chem, Soc*,, 1921, **119**, 379), Selenium tetra-chloride would, therefore, react with the substituted amides of malonic acid to form either chloro-compounds or selenides of the type, $>C{=}Se$.

It is not improbable that in the initial stage of the reaction a diselenide, $:C:Se:Se$ may have been formed, which then passes over into a monoselenide of the type $>C{:}Se$. This is not unusual in view of the mechanism of the reaction between ethylene and sulphur monochloride.

$$2CH_2:CH_2 + Cl_2:S:S < \begin{array}{ll} (CH_2Cl{\cdot}CH_2)_2S:S & (I) \\ (CH_2Cl{\cdot}CH_2)_2S + S & (II) \end{array}$$

That the disulphide (1) passes into the monosulphide (2) was finally settled by the late Lieut. Col. Harrison during the

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* Michaelis and Kunckell, *Ber*, 1897, **30**, 2823; Morgan and Drew, *J. Chem. Soc.*, 1920, **117**, 1456; *ibid*, 1922, **121**, 2441; Morgan and Porte, *ibid*, 1924, **125**, 1272.

great war. The second sulphur atom in this case behaves as if it were in solution (Naik, *loc. cit.*). The same may be held to be true in the case of the selenides.

In the present case it was found that selenium compounds of the type (*b*) $>C:Se$, were only formed. It was also interesting to find out the exact conditions under which selenides could be obtained, as also those governing the formation of the chloro-compounds.

With the above purpose in view selenium tetrachloride was made to react with the following substituted amides :—

(1) Malon-diphenylamide, (2) Malon-di-*p*-tolylamide, (3) Malondi-*m*-tolylamide, (4) Malon-di-β-naphthylamide, (5) Methylmalon-di-phenylamide, (6) Methylmalon-di-*p* tolylamide, (7) Methylmalon-di-*m*-tolylamide, (8) Methylmalon-di-β-naphthylamide (9) Malon-dibenzylamide, (10) Malon-dipropylamide, (11) Malon-diheptylamide, (12) Malon-di-(1 : 3 : 4) xylidide, (13) Malon-di-(1 : 4 : 5) xylidide, (14) Malon-di-*a*-naphthylamide, (15) Malonamide, (16) Malonmonophenylamide, (17) Malonmono-*p*-tolylamide, (18) Malon-*p*-tolylamate, (19) Malonic ester.

The main results of the present investigation can be summarised as under :—

Type I—Amides which interact to form selenides. Compounds from (1) to (8) interact to form selenides of the type,

$(\text{-CO}\cdot\text{C}\cdot\text{CO-})_2$.
(..)
Se

Type II—Amides which interact to form chloro-compounds Compounds from (9) to (13) react to give substances of the type, $\text{-CO}\cdot\text{CCl}_2\cdot\text{CO-}$

Type III—Amides which do not interact with selenium tetrachloride. Substances (14) to (17) do not react.

Compounds (18) and (19) form resinous products with selenium tetrachloride.

Type I.—The first compound of this series was prepared by the action of selenium tetrachloride on malon-diphenyla-

mide in dry ether, at ordinary temperature (27-30°). The course of the reaction can be represented as—

$$5(PhNH{\cdot}CO)_2CH_2+4SeCl_4=5(PhNH{\cdot}CO)_2CH_2 + (2Se_2Cl_2+6Cl_2)$$
$$=\underset{(I)}{2(PhNH{\cdot}CO)_2C:Se}+\underset{(II)}{3(C_6H_4Cl{\cdot}NH{\cdot}CO)_2CH_2}+10HCl+2Se.$$

That the reaction actually follows the course shown above is based on the following considerations :—

(1) Of the malon-diphenylamide used, only a small quantity was utilised to form the selenide (I), as was evident from the yield.

(2) The chloro-compound (II) was obtained in a large yield, though it was very difficult to get it in a pure condition, owing to the presence of free selenium in colloidal condition.

(3) The observations of Taylor, Prideux and Pool regarding the decomposition of selenium tetrachloride (*loc. cit.*) also lend support to the view that the reaction follows the course represented by the equation given above.

That the selenide (I) has the constitution shown above is evident from the following observations;—

(*i*) The two hydrogen atoms eliminated in the formation of the selenide (I) are not those which were originally attached to two nitrogen atoms, because on hydrolysis with aqueous potassium hydroxide, the corresponding derivative of malon-di-β-naphthylamide broke down giving β-naphthylamine.

(*ii*) The above fact also supports the view that the hydrogens eliminated are not those from the nuclei, for if that were so, β-naphthylamine could not be formed during the hydrolysis.

(*iii*) That the hydrogens are only removed from the methylene group in the present interaction is further borne out by the reaction of methylmalon-diphenylamide with selenium tetrachloride, where a selenide of the constitution, $(Ph{\cdot}NH{\cdot}CO)_2C(CH_3){\cdot}Se{\cdot}C(CH_3)(CO{\cdot}NHPh)_2$ is formed. Here the selenium tetrachloride requires two mono-substituted methylene groups

to supply the two necessary hydrogens, in spite of the fact that each molecule of methylmalon-diphenylamide has two hydrogens available either from those attached to the nitrogens or from the two nuclei.

It is evident, therefore, that the formula assigned to the selenide of malon-diphenylamide is correct. On considerations which led Morgan and his co-workers to represent selenium as tetravalent, the selenide (I) of malon-diphenylamide may be represented as—

$$(PhNH{\cdot}CO)_2{:}CSe{:}Se{:}C{:}(CO{\cdot}NHPh)_2.$$

As the selenides so obtained, are all insoluble in ordinary solvents, it was found very difficult to determine the molecular weight of any of these compounds. The stability of these selenides when treated with sodium bisulphite, which should reduce them to the corresponding substituted malonamides, goes to strengthen the view that selenium here is rather tetravalent than divalent,

Returning now to the dichloro-compound (II), one is led to believe that the two chlorine atoms are in the nuclei, for, on trying to reduce the dichloro-compound with hydrogen iodide by Kurt Meyer's method, the dichloro-compound was obtained unchanged. This compound is, therefore, different from the dichloromalon-diphenyl-amide $CCl_2(CO{\cdot}NHPh)_2$ obtained by Naik and Shah (*J. Indian. Chem; Soc.*, 1926 **4**, 12) by the interaction of sulphuryl chloride and malon-diphenylamide. That the two chlorine atoms of compound (II) are in the nuclei is further borne out by the fact that on hydrolysis with aqueous potash it yielded *m*-chloroaniline.†

†That the product of hydrolysis is *m*-chloroaniline is substantiated on the following grounds:—

(*i*) The acetyl (m. p. 71°) and the benzoyl derivatives (m. p. 120°) of the product were found to be identical with those obtained from *m*-chloroaniline.

(*ii*) *p*:*p*-Dichlormalonanilide melts at 261° (Chattaway and Mason, *J: Chem. Soc.*, 1910, 97, 340), whereas our dichloro-compound melts at 175°-76°.

It seems curious that in the compound (II) the halogens should prefer the nuclear hydrogens to those of the reactive methylene group. This behaviour is easily explained on the considerations of the results obtained by Silberrad and Park (*J. Chem. Soc*, 1925, **127**, 2449), who pointed out that in the presence of chlorides of selenium as catalysts, chlorination of benzene derivatives takes place preferably in the nucleus rather than in the side-chain.

From the above it follows that the dichloro-compound (II) should be represented as $CH_2(CONHC_6H_4Cl)_2$.

The constitution of the two main products of the present interaction having been thus established, reactions of other substituted amides with selenium tetrachloride were tried.

Malon-di-*p*- and -*m*-tolylamides and malon-di-β-naphthylamide reacted with selenium tetrachloride giving rise to the selenides of the type $(RNH{\cdot}CO)_2C{:}Se{:}\,Se{:}\,C\,(CO.\,NHR)_2$.

In order to study whether the same, type of reactivity presisted throughout the corresponding derivatives of methylmalonic acid, the following four amides, namely (5) (6), (7), and (8) (*vide supra*) were subjected to the action of selenium tetrachloride, when it was found that selenides of the general structure, $>C(CH_3)Se{\cdot}C,(CH_3)<$ were formed,

It may be noted here that malonamide, malon-monophenylamide and malonmono-*p*-tolylamide were found not to react with selenium tetrachloride. Thus the reactivity which only began to manifest itself in the case of the dianilides and ditolylamides was increasing rapidly in the case of malon-*o*- and *p*-tolylamates, and reached its maximum in the case of malonic ester itself, so much so, that in the last two cases resinous products were obtained. Thus the experimental observations afford a clear evidence that the interaction of selenium tetrachloride with the amides enumerated above depends on the total negativity of the groups attached to the two remaining valencies of the methylene carbon atom. If this carry neutral groups such as—$CONH_2$ as in malonamide, no interaction

occurs. Even when the neutral character of one of the $CONH_2$ group is disturbed by a phenyl or a tolyl group, interaction does not start. But when the neutral character of both the $-CONH_2$ groups is disturbed by converting them into -CONHPh group, the reactivity starts. In a series like.

$CH_2(CO{\cdot}NH_2)_2$ (*i*)	$NH_2COCH_2CONHPh$ (*ii*)	$CH_2(CO{\cdot}NHC_{10}H_7)_2$ (*iii*)
$CH_2(CO{\cdot}NHPh)$ (*iv*)	$CO_2Et{\cdot}CH_2CO{\cdot}NHPh$ (*v*)	and $CH_2(CO_2Et)_2$ (*vi*)

the reactivity which is absent in (*i*) and (*ii*) starts in (*iii*) and goes on increasing, lesser and lesser time being required for the completion of the reaction. Finally in the case of (*v*) and (*vi*) the reaction proceeds so vigorously that resinous products are obtained.

The interaction of selenium tetrachloride with the amides enumerated under Type II, resulted in the formation of dichloro-compounds, thus:

$$(RNHCO)_2CH_2 + SeCl_4 = (RNHCO)_2CCl_2 + 2HCl + Se.$$

In all these cases the halogens replaced the hydrogens originally attached to the methylene carbon atom, as was evident from the fact that when such compounds were treated with potassium iodide and concentrated hydrochloric acid, the halogens were easily reduced. Of the five compounds thus prepared two, namely dichloromalon-dipropylamide and dichloromalon--dibenzylamide were identical with those prepared by Naik and Shah (*loc. cit*). The other three are new and their constitutions are established on the same considerations as in the case of the first two dichloro-compounds. Such a type of chlorinating action of selenium tetra-chloride has already been reported by Morgan and Drew *J. Chem. Soc.*, 1920, **119**, 1452).

EXPERIMENTAL.

General Method of preparation.—The amide (5 mols.) was made to react with selenium tetrachloride (4 mols.) suspended

in anhydrous ether. The reactions were carried out at ordinary temperature carefully excluding moisture. Hydrogen chloride was evolved during the course of the reaction. At the end of the reaction, (usually after 8 or 10 hours) the ether was slowly evaporated off and a greenish-yellow product coated with a thin film of selenium (red variety) was obtained. The dry mass was then repeatedly extracted with dry benzene, till no red film was formed on the product on drying. To ascertain that the compound was free from selenium metal, it was treated with reduced copper gauze in boiling benzene, until the shining surface of the copper gauze no longer blackened. The product was thus completely freed from selenium.

Selenomalon-diphenylamide.—Malon-diphenylamide (1·5 g.) was made to react with selenium totrachloride (1·0 g.) in 50 c. c. of anhydrous ether. Selenomalon-diphenylamide was isolated and purified as mentioned above. The substance was insoluble in alcohol, chloroform, benzene, ether, petroleum, carbon disulphide, carbon tetrachloride, toluene, xylene, acetic acid and acetone. It was soluble in aniline and pyridine, but on evaporating the solvents, the substance was found to have been decomposed into the original malon-diphenylamide and elemental selenium (yellowish-green amorphous powder,) It darkened at 217° and melted at 222-223° to a clear red liquid. (Found: Se, 22·98. $C_{30}H_{24}N_4O_4Se_2$ requires Se, 23·86 per cent.)

Reduction of Selenomalon-diphenylamide.-On reduction with alkaline hydrosulphide (Brand, *Ber.*, 1906, **42**, 3464) selenomalon-diphenylamide was transformed into malon-diphenylamide and hydrogen selenide. The hydrogen selenide thus formed deposited selenium (red variety) on standing, the malon-diphenylamide obtained having been identified.

Bromination of Selenomalon-diphenylamide-When compound (I) was treated with bromine, selenium bromide was produced together with $CBr_2(CO{\cdot}NHPh)_2$, which was found to be identical with the compound of Backes, West and Whiteley (*J. Chem. Soc.*, 1921, **119**, 374).

Malon-dichlorodiphenylamide,—In the course of the above reaction malon--diphenylamide was partly converted into maloudichloro-phenylamide, This substance was obtained in benzene solution, used in the extraction of selenomalon-diphenylamide. On evaporating benzene malon-dichlorodiphenylamide was obtained as a crude sticky red powder. On repeated crystallisation it was obtained in the form of colourless cubic crystals from alcohol, m. p. 175-76°. (Found: Cl, 21·70. $C_{15}H_{12}N_2O_2Cl_2$ requires Cl, 21·96° per cent.)

Hydrolysis of Malon—dichlorodiphenylamide.—The dichloro-compound (2·0 g.) was mixed with an aqueous solution of caustic potash (5 g. NaOH in 10 c. c.). The whole was then refluxed for three hours. A red-brown *liquid* separated. This was extracted with ether, and after purification was identified as *m*-chloroaniline (b. p. 23°).

Selenomalon-di-p--tolylamide.-Malon-di-*p*-tolylamide (1·5 g.) and selenium tetrachloride (1 g.) in 50 c. c. anhydrous ether were employed and the resulting selenomalon-di-*p*-tolylamide was obtained after purification, as an yellow powder, m. p. 218-219°. The behaviour of this substance towards solvents was similar to that of selenomalon-diphenylamide. (Found: Se, 22·09. $C_{34}H_{32}N_4O_4Se_2$ requires Se, 22·01 per cent.).

Selenomalon-di-m—tolylamide.—This was obtained in the same way as the *para*-derivative and had in similar properties, the time required for the completion of the reaction was less in this case. It melted at 210-211°, darkening previously at 205°. (Found: Se, 21·75, $C_{34}H_{32}N_4O_4Se_2$ requires Se, 22·04 per cent.).

Selenomalon—di—β-naphthylamide.—Selenium tetrachloride (1 g.), suspended in 60 c. c. of anhydrous ether was made to react with malon-di-β-naphthylamide (1·3 g.), the reaction mixture being kept overnight, Selenomalon-di-β-naphthyl-amide, m, p. 220°, was obtained after the usual procedure, (Found: Se, 18·26. $C_{46}H_{32}N_4O_4Se_2$ requires Se, 18·32 per cent.),

Hydrolysis-of-Selenomalon-di-β-naphthylamide.—One g. of the selenide was refluxed for two hours with 20 c. c. of alcoholic potash (1 g.) when a buff-coloured solution was obtained. A flocculent white mass separated on pouring the solution into a large excess of water. This was subsequently identified to be β-naphthylamine, m. p. 111°. The filtrate deposited red selenium on standing.

Selenomethylmalon-diphenylamide.–Methylmalon--diphenylamide (2 g.) and selenium tetrachloride (1·5 g.) in 60 c. c. of anhydrous ether were used. The substance resembled the corresponding malon-diphenylamide derivative in its behaviour; m. p. 222-224°. (Found: Se, 12·42. $C_{32}H_{30}N_4O_4Se$ requires Se, 12·87 per cent.).

Selenomethylmalon-di-p-tolylamide.—The amide (2·5 g.) in 25 c. c. of dry ether and selenium tetrachloride (1·0 g.) gave a product which was purified in the usual way. It blackens at 210° and melts at 224·225°. Found: Se, 11·76 $C_{36}H_{34}N_4O_4$ Se requires Se, 11·95 per cent.).

Selenomethylmalon-di-m-tolylamide.—This was obtained in the form of a yellow amorphous powder by the interaction of 2·5 g. of the amide with 1 g. of selenium tetrachloride. It melted at 221°. (Found: Se, 11·63. $C_{36}H_{34}N_4O_4Se$ requires Se, 11·95 per cent.).

Selenomethylmalon-di-β-naphthylamide.—The selenide was prepared in the usual way from 3 g. of the amide and 1·0 g. of selenium tetrachloride. It was a yellow powder insoluble in all organic solvents and melted at 229-230°. (Found: Se, 9·33, $C_{48}H_{42}N_4O_4Se$ requires Se, 9·71 per cent.).

Dichloromalon-diheptylamide.--Malon-diheptylamide (1·5 g) was treated with selenium tetrachloride (1 g.) in 30 c. c. of dry ether. At the end of 10-12 hours, both the amide and the selenium tetrachloride went into solution (pink). On evaporating the solution by means of hot air, a red pasty residue was obtained. On treatment with alcohol the pink film of red selenium was precipitated and a fairly colourless solution of

the dichloro-compound was obtained. After repeated crystallisations, the substance was obtained in colourless, stout, prismatic needles, m. p. 90°. It was soluble in alcohol, chloroform, carbon tetrachloride, benzene, ether, acetic acid and acetone. (Found : Cl, 19·05. $C_{17}H_{32}N_2O_2Cl_2$ requires Cl, 19·34 (per cent.).

Dichloromalon-di-(1 : 3 : 4) *xylidide.*—This substance was obtained from malon-di-(1 : 3 : 4) xylidide (1·8 g.) and selenium tetrachloride (1·0 g.) in 50 c. c. of anhydrous ether. The pure sample formed fine colourless needles melting at 136-137°. (Found : Cl, 18·09. $C_{19}H_{20}N_2O_2Cl_2$ requires Cl, 18·53 per cent.).

Dichloromalon-di-(1 : 4 : 5) *xylidide.*—This was obtained in the same way as the previous xylidide. On crystallisation it was obtained as colourless, shining, short needles, m. p. 170°. (Found : Cl, 18·26. $C_{19}H_{20}N_2O_2Cl_2$ requires Cl, 18·73 per cent.)

The authors desire to express their gratitude to His Highness the Maharaja Gaekwar's Government, for a grant by which the expenses incurred in this research were met.

CHEMISTRY DEPARTMENT,
THE COLLEGE, BARODA.

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XIX. Interaction of Iodine Monochloride with Substances Containing the Reactive Methylene Group.

BY K. G. NAIK AND C. C. SHAH.

Although the chloro- and bromo-derivatives of substituted malonamides have been extensively prepared and studied (Backes, West and Whiteley, *J. Chem. Soc.*, 1921, **119**, 362; West, *ibid*, 1922, **121**, 2196; 1924, **125**, 710; 1925, **127**, 748; Naik and Shah, *J. Indian. Chem. Soc*; 1927, **4**, 11), iodo-derivatives of the same are not known. However, di-iodomalonic acid and methyl di-iodomalonate have been prepared by Willstätter (*Ber.*, 1902, **35**, 1377), who describes them as very unstable substances decomposing spontaneously at ordinary temperature,

Moreover, in view of the fact that the chloromalonamides are more stable than the bromomalonamides (West, *loc. cit.*), it was expected that iodomalonamides will be very reactive and will thus form an interesting subject for the study of the effect of the adjoining groups on the two hydrogen atoms of the reactive methylene group, which problem is being tackled in this laboratory for the last several years (Naik, *J. Chem. Soc.*, 1921, **119**, 379 and subsequent papers).

With this end in view, the interaction of iodine monochloride with the following substances was studied:—

(1) Malondipropylamide, (2) malondiheptylamide, (3) malon-amide, (4) malondibenzylamide, (5) malondiphenyl-amide, (6) malondi-*o*-tolylamide, (7) malondi-*p*-tolylamide, (8) malon-dimethylphenylamide, (9) malondi-*α*-naphthyl-amide, (10) malonmonophenylamide, (11) malonmono-*p*-tolylamide, (12) methylmalon-diphenylamide, and (13) methyl-malondi-*o*-tolylamide.

The use of iodine monochloride as an iodinating agent is well known (Schützenberger, *Z. Chem. pharm*; 1861, **5**, 1; Michael and Norton, *Ber*; 1878, **11**, 108; Ostermeyer, C, **1884**, 937; Wheeler and Liddle, *Amer. Chem. J.* 1909 **42**. 441; C; **1910. I**, 528; Willgerodt and Arnold, *Ber*; 1901, **84**, 3344; Cofman, *Gazzetta* 1920, II, **50**, 269; C; **1921**, **I**, 943) specially in the case of aromatic compounds. It was expected that here also, iodo-derivatives of the substituted malonamides will be obtained. But contrary to our expectations we only obtained chloro-derivatives many of which have already been prepared by Naik and Shah (*loc. cit.*).

Of the compounds investigated, in the case of (1), (2), (3), (4), (6), (7) and (11), the reactive methylene group was converted into -CCl_2 without the halogenation of the nucleus, while in the case of (9), the nucleus was also attacked and $CCl_2(CO{\cdot}NHC_{10}H_6Cl)_2$ was obtained. In the case of (8) and (10); only one hydrogen atom of the methylene group was attacked with the formation of the—CHCl group, the nuclei

in the case of (8) remaining un-affected. In the case of (12) and (13), having only one available hydrogen in the methylene group; Me CCl $(CO{\cdot}NHC_6H_4Cl)_2$ and MeCCl $(CO{\cdot}NHC_7H_6Cl)_2$ were formed.

Malon-diphenylamide (5) forms a curious exception for in this case the methylene group remains intact, the nuclei only being halogenated, giving rise to $CH_2(CO{\cdot}NHC_6H_4Cl)_2$. The same compound was obtained by Naik and Trivedi *J. Indian Chem Soc.*, 1930, **7**, 239) by the action of selenium tetrachloride on the same substance.

The method for differentiating the chlorine atoms in the methylene group from those in the nucleus was the same as the one adopted by Naik and Shah (*loc. cit.*).

EXPERIMENTAL.

The amide (1 mol.) was treated with iodine monochloride (4 mols.) in presence of chloroform. After allowing the reaction mixture to remain at ordinary temperature (30°) for twenty-four hours, it was refluxed on a water-bath for three hours. The chloroform solution was then shaken with 10 per cent. sodium thiosulphate to remove free iodine and after separation from the aqueous layer was evaporated to dryness. The resulting solid was crystallised from a suitable solvent. In the case of dichloromalonamide, nothing was recovered from the chloroform solution, so the white mass adhering to the flask was extracted with water, and was boiled till all the iodine volatilised; the solution was then concentrated when the product separated.

In this way, malon-dipropylamide gave rise to dichloro-malon-dipropylamide (Naik and Shah), malondiheptylamide to dichloro-malondiheptylamide (Naik and Trivedi), malonamide to dichloromalonamide (Backes, West and Whiteley) malondibenzylamide to dichloromalondibenzylamide (N. and S.), malondiphenylamide to malondichlorophenylamide (N. and T.), malondi-*o*-tolylamide to dichloromalondi-*o*-tolylamide (N. and S.), malondi-*p*-tolylamide to dichloromalondi-*p*-

tolylamide (N. and S.), malondimethylphenylamide to monochloromalondimethylphenylamide (N. and S.), and malonmono-*p*-tolylamide to dichloromalonmono-*p*-tolylamide (N. and S.).

Dichlonomalondichloro-∝-naphthylamide was obtained from one g. of the amide and 4 g. of iodine monochloride. It was recrystallised from benzene as white needles, m.p. 191°. It is fairly soluble in alcohol, benzene and chloroform but slightly so in petroleum. (Found : Cl, 28·71; Cl(malonyl). 14·44 $C_{23}H_{14}O_2N_2Cl_4$ requires Cl, 28·92; Cl (malonyl) 14·46 per cent.)

Monochloromalonmonochlorophenylamide :—One g. of the amide and 3 g. of iodine monochloride in 25 c. c. of chloroform were taken. The white substance was crystallised from benzene, m.p. 152°.

It is easily soluble in alcohol, benzene, chloroform and acetic acid but almost insoluble in light petroleum. (Found : Cl,28·35; Cl, (malonyl), 14·80. $C_9H_8O_2N_2Cl_2$ requires Cl, 28·86; Cl (malonyl), 14·43 per cent.).

Methylchloromalondichloro-phenylamide—One g. of methylmalondiphenylamide and 4 g. of iodine monochloride were used. The product separated from benzene; m. p. 164°. It is very soluble in chloroform, acetone and ether but less so in benzene and alcohol. (Found : Cl, 28.31; Cl (malonyl), 9·74. $C_{16}H_{13}O_2N_2Cl_3$ requires Cl, 28·67; Cl (malonyl), 9·55 per cent.).

Methylchloromalondichloro-o-tolylamide was obtained by the interaction of 3·5 g. iodine monochloride with 1 g. methylmalondi-o-tolylamide in 25 c. c. chloroform. It crystallises in fine needles from benzene and melts at 184°. It is very soluble in acetone but less so in benzene, alcohol and chloroform, and insoluble in petroleum. (Found : Cl, 26·74; Cl (malonyl), 9·31. $C_{18}H_{17}O_2N_2Cl_3$ requires Cl, 26·62; Cl (malonyl), 8·88 per cent.).

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CHEMISTRY DEPARTMENT, BARODA COLLEGE.

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XX Mercuration of Compounds Containing the Reactive Methylene Group.

BY K. G. NAIK AND C. C. SHAH.

The mercuration of the substiuted amides of malonic acid was undertaken with a view to study the change in the stability of the carbon-mercury linkage in these compounds and thus throw, if possible, some light on the effect of the adjoining groups on the reactivity of the two hydrogen atoms of a methylone group situated between two negative groups, which has been the subject of investigation by Naik and his collaborators (Naik, *J. Chem. Soc.*, 1921, **119**, 379 and subsequent papers).

We have employed the method of Neogi and Chatterjee (*J. Indian Chem. Soc.*, 1928, **5**, 221), the mercurating agent being mercuric chloride in presence of sodium bicarbonate and glycerol. It may be that at first an oxychloride of mercury is formed, which subsequently reacts with the organic compounds giving rise to a mercurated product, thus:—

$$HgCl_2 + NaHCO_3 = Hg(OH)Cl + NaCl + CO_2$$
$$R{\cdot}H + Hg(OH)Cl = R{\cdot}HgCl + H_2O.$$

The following compounds were mercurated by this method:—(1) Malonamide, (2) malondimethylamide, (3) malondiethylamide, (4) malondipropylamide, (5) malondi-*n*-butylamide, (6) malondi*iso*butylamide, (7) malondi*iso*amylamide, (8) malondiamylamide, (9) malondiheptylamide, and (10) ethyl malonate.

Of these (7) and (8) were prepared for the first time. Only the alkylamides of malonic acid were selected for the present purpose, in order to avoid the complications that may occur by the entrance of mercury in the nuclei of arylamides.

All the substances enumerated above react with mercuric chloride under the experimental conditions yielding products having the general formula.

$$\begin{matrix} R\cdot CO \\ R\cdot CO \end{matrix}\!\!>C<\!\!\begin{matrix} HgCl \\ HgCl \end{matrix}$$

where R=ethoxy; amino-, methylamino-, etc. group.

This constitution has been assigned to the compounds from the following considerations—

(*i*) The mercury has not entered the aliphatic part of the amido-group (-NHR) because—

(*a*) no example seems to have been recorded in literature of mercury having thus substituted a hydrogen atom of an aliphatic compound;

(*b*) malonamide, which contains no such aliphatic part, forms a similar mercury derivative;

(*c*) the mercury derivatives of aliphatic compounds are not easily decomposed by potassium iodide and hydrochloric acid, while dichloromercurimalondiheptylamide, obtained during the course of this work, is attacked by these reagents giving the original amide.

(*ii*) The mercury atom has not replaced the *N*-hydrogen atom, for

(*a*) malonic ester which contains no such hydrogen atom forms a similar compound with mercuric chloride;

(*b*) a study of the known mercurated *substituted* amides shows that the hydrogen attached to nitrogen can be substituted by mercury under exceptional conditions. Acetanilide on fusion with mercuric oxide forms *N*-mercuri-bis-acetanilide (Oppenheim and Paaff, *Ber.*, 1874; **7**, 624, Wheeler, *Amer. Chem. J*; 1896, **18**, 696; Pesci, *Gazzetta*, 1897, I, **27**; 568), though a boiling solution of acetanilide gives *p*-acetaminophenylmercuric acetate (Pesci, *Z. anorg. Chem.*, 1897, **15**, 222; Dimroth, *Ber*; 1902, **35**, 2037). Similarly *p*-acetoxymercuri-*o*-acetotoluidide is formed by refluxing *o*-acetotoluidide with mercuric acetate in water (Schrauth, Schoeller and Rother,

Ber., 1912, **45**, 2812) while no *N*-mercury-derivative of the same seems to have been reported. Similar results are obtained with *m*-and *p*-acetotoluidides;

(*c*) the *N*-Hg-compounds behave as weak bases and a solution of mercuri-acetamide can be titrated with hydrochloric acid using methyl orange as indicator (Ley and Kissel, *Ber.*, 1899, **32**, 1357), while the products obtained here are decomposed rather slowly.

(*iii*) The mercury is directly attached to the methylene carbon atom, for—

(*a*) dichloromercurimalonamide gives dibromomalonamide on treatment with bromine;

(*b*) the properties and behaviour of the products obtained is the same as those of compounds having mercury attached to the carbon in α-position to a keto-group, as is shown below.

The stability of the carbon-mercury bond varies over a very wide range. Thus, in contrast to some of the mercarbides which remain unchanged even after prolonged boiling with fuming hydrochloric acid (Hofmann, *Ber.*, 1898, **31**, 1905; 1900, **33** 1336), substances having a mercury atom attached to a carbon atom in α-position to a keto-group, lose it on treatment with 0·25*N*-hydrochloric acid (Dimroth, *Ber.*, 1902, **35**, 2870).

Ethyl dichloromercurimalonate $(HgCl)_2:C:(CO_2Et)_2$, which was also prepared by Biilmann (*Ber.*, 1902, **35**. 2580), on treatment with hot concentrated hydrochloric acid, liberates mercuric chloride and forms ethyl monochloromercurimalonate, thus :

$$(HgCl)_2 : C : (CO_2Et)_2 + HCl = HgCl \cdot CH : (CO_2Et) + HgCl_2.$$

It is rather curious to observe that the second mercury atom in the same position is not removed simultaneously. This behaviour is not, however, quite abnormal, for bromomercuri-acetic acid, $BrHg \cdot CH_2 \cdot CO_2H$, which contains a mercury atom attached to a carbon atom in α-position to a keto group, is not decomposed by acids (Hofmann and Sand, *Ber.*, 1900, **33**, 1346)

In the case of dichloromercurimalondiheptylamide, on the other hand, both the chloromercuri-groups are removed by the action of hydrochloric acid.

It has also been possible to obtain ethyl monochloromercurimalonate by the action of *cold* aqueous potassium iodide on the dichloromercuri-ester, though both the chloromercuri-groups are removed by the action of *hot* potassium iodide solution. Potassium iodide reacts with organo-mercury compounds of the type R·HgX in three different ways: (*i*) it may give rise to compounds of the type R·HgR (Whitmore, *J. Amer Chem. Soc.*, 1919, **41**, 1850); (*ii*) it may form an iodomercuri-compound, R·HgI (Volhard, *Annalen*, 1892, **267**, 172), or (*iii*) it may bring about a complete splitting up of the carbon-mercury linkage with the liberation of one equivalent of alkali for each carbon-mercury linkage, thus :

$$R{\cdot}HgX+KI+H_2O=R{\cdot}H+HgXI+KOH.$$

All compounds having mercury substituted for the hydrogen atoms in the grouping. $-CO{\cdot}CH_2{\cdot}CO-$, $-CO{\cdot}CH_2{\cdot}CN$, etc., behave in the above manner (Biilman, *Ber.*, 1902, **35**, 2580; Biilmann and Witt, *Ber.*, 1909, **42**, 1070; Petterson, *J. pr. Chem.*, 1912, *ii*, **86**, 464). Dichloromercurimalondiheptylamide is also decomposed by potassium iodide, with the liberation of two equivalents of alkali.

The substances containing mercury in the reactive methylene group are unusually reactive towards hydrogen sulphide immediately giving mercuric sulphide (Biilmann, *loc. cit.*; Biilmann and Witt, *loc. cit.*, Lippmann, *Z. Chem.*, 1869, *ii*, **5**, 29 ; Oppenheim, *Ber.*, 1877, **10**, 701 ; Behrend, *Z. phaysikal. Chem.*. 1893, **11**, 478 ; Hofmann, *Ber.*, 1898, **31**, 2215 ; Ley, *Ber.*, 1900, **33**, 1014 ; Michael, *Ber.*, 1905, **38**, 2090); ethyl dichloromercurimalonate instantaneously gives a black precipitate of mercuric sulphide on treatment with hydrogen sulphide.

Sodium thiosulphate is the most general reagent used to bring about a change from the organo-mercury compounds of the type R·HgX to compounds of the type $R_2{:}Hg$ (Pesci,

Gazetta, 1899, I, **29**, 394; Dimroth. *Ber.*, 1908, **35**, 2041; Kharasch and Piccard, *J. Amer. Chem. Soc.*, 1920, **42**, 1861: Whitmore and Middleton, *ibid*, 1921, **43**, 622, etc.). However, when ethyl dichloromercuri-malonate was dissolved in concentrated sodium thiosulphate solution, only a negligible amount of a red substance was deposited after standing for a day.

Freund (*Ber.*, 1884, **17**, 133) obtained a compound from malonamide and mercuric oxide to which he assigned the formula $CH_2 : (CONH)_2 : Hg$, because dibromomalonamide also gives a similar compound, $CBr_2 : (CONH)_2 : Hg$ (Freund *Ber.*, 1884, **17**, 785). However for the aforesaid reasons, dichloromercurimalonamide has been assigned the formula $(ClHg)_2 : C : (CONH_2)_2$.

It has been observed by Naik and his co-workers that in a series like—

(*i*) $CH_2(CO{\cdot}NH_2)_2$ (*iv*) $RNH{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$
(*ii*) $RNH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH_2$ (*v*) $CN{\cdot}CH_2{\cdot}CO_2Et$
(*iii*) $CH_2(CO{\cdot}NHR)_2$ (*vi*) $CH_2(CO_2Et)_2$

the reactivity of the methylene hydrogen atoms increases from (*i*) to (*vi*). In it be assumed that the chloromercuri group which replaces a hydrogen atom of the methylene group is attached to the carbon atom with the same degree of tenacity as the corresponding hydrogen atoms, then the decomposition of the chloromercuri-derivatives of such compounds by potassium iodide, etc., will also be in the order of this reactivity. This has actually been found to be the case, for dichloromercurimalondiheptylamide reacts with potassium iodide more slowly than does ethyl dichloromercurimalonate.

Mercury in these compounds was estimated by the Francois' method; while chlorine was estimated by the Carius' method, but the precipitate of silver chloride was filtered and washed in the cold, on account of the solubility of silver chloride in hot water in the presence of mercuric salts.

EXPERIMENTAL.

Ethyl Dichloromercurimalonate.—Ethyl malonate (2 g.) and mercuric chloride (7 g.) were dissolved in dilute (30%)

alcohol and glycerol (20 c.c.) added. A solution of sodium bicarbonate (2·5 g.) was slowly added to it with constant stirring. After some time small silky needles began to come down. These were filtered after two hours and repeatedly washed with dilute alcohol. The substance is insoluble in any of the ordinary solvents. It does not melt below 300°. (Found : Hg, 61·10; Cl, 11·44. $C_7H_{10}O_4Cl_2Hg_2$ requires Hg, 63·59; Cl, 11·28 per cent.).

Action of Hydrochloric Acid on the above.—The substance (1 g.) was suspended in dilute alcohol and concentrated hydrochloric acid (10 c. c.) added. After refluxing for half an hour, the residue was filtered and washed. The filtrate was found to contain mercuric chloride. The substance was insoluble in any solvent and does not melt but turns grey at 192-5°. (Found : Hg, 50·93 ; Cl, 8·52. $C_7H_{11}O_4ClHg$ requires Hg, 50·69 ; Cl, 8·92 per cent.)

Action of Hydrogen Sulphide.—When hydrogen sulphide was slowly passed into a hot alcoholic suspension of the substance, a black precipitate of mercuric sulphide was obtained.

Action of Sodium Thiosulphate.—The substance completely went into solution in a 50% solution of sodium thiosulphate. On standing for twenty-four hours, a very small amount of a red substance was deposited.

Action of Potassium Iodide—(a) *Alcoholic.* The compound (0·2036 g.) was suspended in alcohol and potassium iodide (2 g.) added. After half an hour, the alkali liberated, required 3·4 c.c. of 0·098*N*-hydrochloric acid. It was then refluxed for four hours on a water-bath, when a further amount of alkali equivalent to 3·2 c.c. of 0·098*N*-hydrochloric acid was liberated.

		Calc.	Found.
Equivalent of alkali	...	1	1·03
		2	1·99

(b) *Aqueous.* The substance was shaken for half an hour with an aqueous solution of potassium iodide, and the residue was filtered and washed with alcohol. On analysis it was

found to be identical with ethyl monochloromercurimalonate. (Found : Hg, 51·15 ; Cl, 9·23 per cent).

Dichloromercurimalonamide.—Malonamide (2 g.) and mercuric chloride (11 g.) were dissolved in water, and glycerol (20 c.c.) was added. An aqueous solution of sodium bicarbonate (4 g.) was then added to it. After an hour the whole liquid became slightly yellowish. The yellow floating particles coagulated and were easily filtered. The filtrate that came down was a milky solution containing the product in colloidal suspension. It was, therefore, allowed to stand for five days, when the colloidal mass came down in small cubic crystals. This was filtered and repeatedly washed with water.

It is soluble in alcohol, benzene and ether; the pure substance shrinks at 191-2° and melts with decomposition at 220°. (Found: Hg, 70·5; Cl, 12·32. $C_3H_4O_2N_2Cl_2Hg_2$ requires Hg, 70·05; Cl, 12·43 per cent.)

Action of Bromine on the above-Aqueous bromine was slowly added to a suspension of the compound in water, till it was no longer absorbed. The residue was filtered and recrystallised from alcohol; m. p. 203°. It is identical with dibromomalonamide.

Dichloromercurimalondiethylamide.—It was prepared by a similar process. It is soluble in chloroform, benzene, methyl alcohol and ethyl alcohol, and melts at 241° (decomp). (Found Hg, 66·6; Cl, 11.90. $C_5H_8O_2N_2Cl_2Hg_2$ requires Hg, 66·77; Cl, 11·85 per cent.)

Dichloromercurimalondiethylamide—This was prepared by the same method, but in dilute alcoholic solution. It crystallised after three days in cubic crystals. It is soluble in ether, benzene, chloroform and alcohol and has no definite melting point but decomposes turning yellow at 191°. (Found: Hg, 63·5; Cl, 11·65. $C_7H_{12}O_2N_2Cl_2Hg_2$ requires Hg, 63·79; Cl, 11·32 per cent.)

Dichloromercurimalondipropylamide—This was si[illegible]rly prepared. The product was separated on the next day. [illegible] does not crystallise like the foregoing members [illegible]llowed to

remain longer in contact with the solution, but instead gelatinises, which can neither be filtered nor separated. It is soluble in alcohol, ether, chloroform and benzene; it changes colour at 162° and melts at 173-5°. (Found: Hg, 61·5; Cl, 10·72; $C_9H_{16}O_2N_2Cl_2Hg_2$ requires Hg, 6106; Cl, 10·84 per cent.).

Dichloromercurimalondibutylamide.—Prepared in the same way as above, it was washed with dilute alcohol, as it has a tendency to gelatinise in presence of ordinary solvents. This property is also shared by the following products. It is soluble in alcohol , ether, and benzene; m. p. 90°. (Found: Hg, 58·4; Cl, 9·95. $C_{11}H_{20}O_2N_2Cl_2Hg_2$ requires Hg, 58·56; Cl, 10·39 per cent.)

Dichloromercurimalondiisobutylamide.—It was separated on the next day. It is soluble in alcohol, ether, benzene and chloroform; m. p. 108-9° (Found: Hg, 58·8; Cl, 10·52. $C_{11}H_{20}O_2N_2Cl_2Hg_2$ requires Hg, 58·56; Cl, 10·39 per cent.)

Preparation of Malondiamylamide.—This was prepared by the same method as used by Backes,, West and Whiteley (*J. Chem. Soc*; 1921, **119**, 359) for the preparation of alkylmalonamides. Ethyl malonate (8 g.) and amylamine (8.7g.) were mixed up in a sealed tube and allowed to remain at ordinary temperature for 24 hours, and then heated at 120°, for six hours. After cooling, the solid was washed out with petroleum and recrystallised from benzene m. p. 126° (yield, 80 %). It is very soluble in benzene, alcohol, ether, chloroform and carbon tetrachloride but slightly so in petroleum. (Found N, 12·0. $C_{13}H_{26}O_2N_2$ requires N, 11·57 per cent.)

Dichloromercurimalondiamylamide.—The product became quite granular within three hours and could therefore be separated. It was converted into a gelatinous product even on standing for a day. It melts with decomposition at 143°. (Found. Hg, 56·5; Cl. 9·94. $C_{13}H_{24}O_2N_2Cl_2Hg_2$ requires Hg, 56·25; Cl, 9 98 per cent.)

Malondiisoamylamide—Amylamine (9 g.) and ethyl malonate (8 g.) were mixed up in a sealed tube and allowed to remain for a day. This was, afterwards, heated for 12 hours at

200°. The contents were taken out and concentrated on a water-bath, when a thick syrupy liquid was obtained. This was allowed to remain at ordinary temperature for three days, when long needles separated. There were separated by washing with the least amount of petroleum and recrystallised from benzene (yield, 20%).

It is very soluble in alcohol, benzene, chloroform. ether and acetic acid but less so in petroleum and water; m. p. 55°. (Found:N, 12·1. $C_{13}H_{26}O_2N_2$ requires N, 11·57 per cent.)

Dichloromercurimalondiisoamylamide—It was prepared from malondi*iso*amylamide. It is soluble in alcohol, benzene, chloroform and ether; m. p. 105°. (Found: Hg, 56·3; Cl, 9·85. $C_{13}H_{24}O_2N_2Cl_2Hg_2$ requires Hg, 56·25; Cl, 9·98 per cent.)

Dichloromercurimalondiheptylamide.—This was prepared like the other compounds and separated after two hours; m. p. 117°. (Found : Hg, 52.4; Cl, 9.50. $C_{17}H_{32}O_2N_2Cl_2Hg_2$ requires Hg, 52.15;Cl,9.25 per cent.)

Action of Alcoholic Potassium Iodide on the Above—The dry substance (0·1898 g.) was suspended in alcohol and an alcoholic solution of potassium iodide (2 g.) was added. Even after two days an amount of alkali equivalent to 1·5 c. c. of 0·098 *N*-hydrochloric acid was liberated. It was then refluxed for six hours, when the total amount of alkali liberated was found to be equivalent to 5 c. c. of 0·098*N*-hydrochloric acid.

	Calc.	Found.
Equivalent of alkali ..	2	1·97

Action of Hydrochloric Acid.—The substance (0·5 g.) was suspended in water and 1 c.c. of concentrated hydrochloric acid was added. On heating for fifteen minutes a white substance was obtained which was crystallised from alcohol and found to be identical with malondiheptylamide.

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The authors are also grateful to Dr. P. Neogi of Presidency College, Calcutta, for having allowed them to extend his method of mercuration in this investigation.

CHEMISTRY DEPARTMENT,
BARODA COLLEGE,-BARODA.

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XXV. Mercuration of Compounds containing the Reactive Methylene (-CH_2-) group by means of Mercuric Acetate.

BY : K. G. NAIK AND R. P. PATEL.

The mercuration of the substituted amides of acetoacetic acid and malonic acid was undertaken with a view to study the formation and the properties of the organo-mercury derivatives of compounds containing a reactive methylene group, and throw light, if possible, on the reactivity of the hydrogen atoms of a reactive methylene (-CH_2-) group situated between two carbonyl groups.

With this end in view, mercuric acetate was allowed to react in methyl alcohol with the following substances:

(1) Acetoacetanilide, (2) acetoacet-*o*-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet-*p*-toluidide, (5) acetoacet-*α*-naphthyl-amide, (6) acetoacet-*β*-naphthylamide, (7) acetoacet-1 : 3 : 4-xylidide, (8) acetoacet-1 : 4 : 5-xylidide, (9) ethyl acetoacetate, (10) acetoacet-*m*-nitranilide, (11) ethyl malonate, (12) malon-mono-phenylamide, (13) malonmono-*o*-toluidide, (14) malon-mono-*m*-toluidide, (15) malonmono-*p*-toluidide, (16) malon-mono-*α*-naphthylamide, (17) malonmono-*β*-naphthylamide, (18) malonmono-1 : 3 : 4-xylidide, (19) malonmono-1 : 4 : 5-xylidide and (20) malonamide.

Of these (18) and (19) were prepared for the first time by the modification of Whiteley's method (*J. Chem. Soc.* 1903, **83**, 24).

It has been found that when mercuric acetate reacts with aromatic compounds, it introduces very easily the acetoxy-mercury (CH_3-COOHg—) group in the nucleus. It was, there-

fore, expected that in these reactions also, it would not only attack the methylene group, but also attack the aromatic part of these amides. Contrary to our expectations, it was found that mercuric acetate attacked the methylene group only, leaving the aromatic nucleus unaffected, even when mercuric acetate was employed in excess.

Whereas, the amides (1—11) reacted with mercuric acetate in methyl alcohol giving diacetoxymercury derivatives of the formula (I); the amides (12—20) reacted under similar conditions, giving compounds of the general constitution (II).

$$\begin{array}{ccc} CH_3COOHg & & COCH_3 \\ & >C< & \\ CH_3COOHg & & CONHR \end{array} \qquad \begin{array}{ccc} CH_3COOHg & & CONH_2 \\ & >C< & \\ HOHg & & CONHR \end{array}$$

(where R a is H, Phenyl, tolyl, or naphthyl etc. group).

All the above compounds are decomposed by dilute 0·25*N*-hydrochloric acid with the separation of the original amide. Hydrogen sulphide and ammonium sulphide decompose them with the percipitation of black mercuric sulphide. Potassium iodide decomposes the compounds with the liberation of alkali hydroxide. From these reactions, it appears that the linkage between the carbon atom of the reactive methylene group and mercury is a very weak one as is expected from compounds containing mercury attached to a carbon atom in *a*-position to a carbonyl group.

The general constitutions given to the above mercury compounds have been assigned from the following considerations.

(*i*) That the substituted group containing mercury has not replaced the hydrogen atom attached to a nitrogen atom of the ·NHR group (*i. e.*, it does not contain the N—Hg linkage), because, (*a*) malonic ester and acetoacetic ester which do not contain such a nitrogen atom do form similar compounds with mercuric acetate; (*b*) a compound containing N—Hg linkage behaves as a weak base, so much so, that its solution may be easily titrated against standard acid, using methyl orange as the indicator (*cf.* Ley and Kissel, *Ber.*, 1899, **32**. 1357).

(*ii*) That the substituted grouping containing mercury has not replaced the aliphatic part of the molecule, for, (*a*) malonamide which does not contain such an aliphatic group, forms a similar mercury compound; (*b*) mercury compounds of aliphatic amines are not easily decomposed by dilute hydrochloric acid, potassium iodide, and hydrogen sulphide; whereas the compounds described here are easily decomposed by these reagents giving the original amide.

(*iii*) That the substituted grouping containing mercury has not replaced the hydrogen atom of the nucleus, because, (*a*) malonamide, ethyl malonate and ethyl acetoacetate which do not contain such a nucleus, do form similar compounds; (*b*) from literature on mercury compounds, it appears that the mercury atom in the nucleus is not removed by dilute hydrochloric acid, potassium iodide and hydrogen sulphide (*cf.* Schrauth and Bauerschmidt, *Ber.*, 1914, **47**, 2740), while the mercury in these compounds is easily removed.

(*iv*) That the substituted grouping containing mercury is directly attached to the carbon atom of the methylene group, situated between two carbonyl groups, for. (*a*) the properties and the behaviour of compounds described here, are exactly similar to those having mercury attached to a carbon atom in α-position to a carbonyl group. It has been observed in case of mercurated 5- pyrazolone (which contains four acetoxymercury groups) that the mercury in position-4 (*i. e.*, attached to a carbon atom in a position to a carbonyl group in position-5) is easily removed by dilute hydrochloric acid and hydrogen sulphide, the other three acetoxymercury groups, keeping firmly to their positions in the molecule (Schrauth and Bauerschmidt, *loc. cit.*). (*b*) On bromination of acetoxyhydroxymercurimalonamide, dibromomalonamide is obtained.

Mercury compounds of the type (I) react with 10 p. c. sulphuric acid giving compounds of the following constitution:

$$SO_4\!\!<\!\!\begin{matrix}Hg\\Hg\end{matrix}\!\!>\!\!C\!\!<\!\!\begin{matrix}COCH_3\\CONHR\end{matrix}$$

They also react with an aqueous solution of potassium iodide with the separation of the original amide and the liberation of potassium hydroxide. The potassium hydroxide, liberated was found to be 2·013 equivalents, which according to theory should be 2 equivalents. These facts completely prove the constitution assigned to the compounds of the type (I).

Mercury compounds of the type (II), react with standard sodium hydroxide solution, giving a dihydroxymercury derivative.* The quantity of sodium hydroxide required to completely hydrolyse the acetoxymercury ($-CH_3COOHg-$) group was found to be 1·12 equivalents which according to theory should be 1 equivalent. The constitution is further supported by the behaviour of the compounds with sulphuric acid. They give rise to hydroxysulphatomercury derivatives of the following constitution.

$$\begin{array}{ccccccc} NH_2CO & & Hg & —SO_4— & Hg & & CONH_2 \\ & >C< & & & & >C< & \\ RNHCO & & HgOH & & HOHg & & CONHR \end{array}$$

When hydroxyacetoxymercuri-*o* toluidide is, however, made to react with an aqueous solution of potassium iodide, 2·97 equivalents of potassium hydroxide are liberated, which according to the theory should be 3 equivalents. This lends a further strong support to the correctness of the constitution assigned.

EXPERIMENTAL.

Diacetoxymercuriacetoacetanilide.—Mercuric acetate (3·6 g.) dissolved in methyl alcohol, was added to a methyl alcohol solution of acetoacetanilide (1 g.). The solution though clear at first became turbid on heating on a sand-bath for about 10 minutes. On cooling, a snow white crystalline product separated out. It was filtered and washed with water, alcohol and ether to remove the unreacted constituents. The product was insoluble in most of the ordinary organic solvents. It melts with decomposition at 204°. (Found: N, 2·23; Hg, 57·26. $C_{14}H_{15}O_6NHg_2$ requires N. 2·02; Hg, 57·72 per cent.).

The rest of the mercury derivatives have been similarly prepared by the interaction of mercuric acetate with the respective amides in methyl alcohol. The results are given in Table I.

Action of dilute hydrochloric acid.—The above mercury compound decomposed by hot 0·25*N*-hydrochloric acid with the separation of the original amide and mercuric chloride.

Action of potassium iodide.—The above compound (0·2627 g.) suspended in water, was treated with a solution of potassium iodide (1 g.). Potassium hydroxide was at once liberated and titrated against 0·0574*N*-hydrochloric acid (of which 13·3 c. c. were required). It was subsequently heated for about 1 hour, but no further liberation of potassium hydroxide was observed.

Action of hydrogen sulphide.—The above mercury compound (0·491 g.) was suspended in water and heated to boiling. A slow current of hydrogen sulphide gas was passed into the solution till the complete precipitation of mercuric sulphide. Precipitates were then filtered through a Gooch crucible and washed with water, pyridine, carbon disulphide and alcohol to remove the amide formed during the course of the reactions as well as the sulphur which might have precipitated together with mercuric sulphide. It was then dried at 105-10°, and weighed (0·33 g.). Found: Hg, 57·9 $C_{14}H_{15}O_6NHg_2$ requires Hg, 57·72 per cent.).

This indicated that the splitting up of the carbon—mercury linkage by hydrogen sulphide was quantitative.

Action of phenylhydrazine.—The substance decomposed on treatment with phenylhydrazine with the separation of grey metallic mercury.

Sulphatomercuriacetoacetanilide.—The above mercury compound (2 g.) was heated with 10 p. c. sulphuric acid on sand-bath for about ½ hour. It was then cooled, filtered and washed with water alcohol and ether. The product was insoluble in most of the ordinary organic solvents. It turned brown at 240° but did not melt till 300°. (Found: Hg, 59·20; SO_4, 14·55. $C_{10}H_9O_6NSHg_2$ requires Hg, 59·61; SO_4, 14·3 per cent.).

Compounds similar to the above have been prepared by the action of sulphuric acid on compounds 1,2,3,9,12, and 20 of Table I.

The results are given in Table II. Compounds are numbered as 1a, 2a, 3a, 9a, 12a, and 20a.

Action of potassium iodide on diacetoxymercuriacetoacet-o-toluidide.—Diacetoxymercuriacetoacet-*o*-toluidide (1 g.) was treated with potassium iodide in water and heated to boiling. The liberated alkali was neutralised and the solution concentrated and cooled when crystalline needles of acetoacet-*o*-toluidide separated, m. p. 107°.

Action of dilute sodium hydroxide on acetoxymercurimalonmonophenylamide.—The mercury compound (0·5038 g.) was treated with 50 c. c. of 0·018*N*-sodium hydroxide solution and refluxed for ½ hour. It was cooled, filtered and washed with water. The filtrate was then acidified with 10 c. c. of 0·1*N*-oxalic acid to neutralise the unreacted sodium hydroxide. The excess of oxalic acid was titrated against 0·018 *N*-sodium hydroxide (55 c. c.).

The insoluble product was found to be dihydroxymercurimalon-monophenylamide. (Found Hg, 65·1. $C_9H_{10}O_4N_2Hg_2$ requires Hg. 65·57 per cent.).

Action of potassium iodide on Acetoxyhydroxymercurimalonmono o-toluidide. Acetoxyhydroxymercurimalonmono-*o*-toluidide (0·2127 g.) was treated with potassium iodide (1 g.) in water and boiled for 4 hours. The liberated alkali was neutralised by 0·0574 *N*-hydrochloric acid (16·5 c. c.).

Malonmono-1 : 3 : 4-xylidide.—This was prepared by the modification of Whiteley's method (*loc. cit.*). Ethyl malonate (30 g.) and 1 : 3 : 4-xylidine (15 g) were put in a flask, fitted with a cork through which passed a long bent tube and heated in paraffin-bath, at 120·25°. To get the maximum yield, the temperature was not allowed to go beyond 125°. After 8 hours, the contents of the flask were transferred to a glass-stoppered bottle and shaken for 4 hours with twice its volume of ammonia (*d* 0.88). The semi-solid mass was then allowed

to evaporate and the residue was pressed on a filter and finally washed with ether to remove any of the unreacted ester and amine. It was then boiled with dilute alcohol (1:6) and filtered hot. The dixylidide and xylylamate remained on the filter undissolved. The filtrate on cooling separated malonmono-1 : 3 : 4-xylidide. The product when crystallised from the same solvent melts at 166°.

It is very soluble in methyl alcohol, ethyl alcohol, acetic acid, hot water, and sparingly soluble in cold water, hot benzene, but practically insoluble in petroleum. (Found: N, 13·57. $C_{11}H_{14}O_2N_2$ requires N, 13·59 per cent.).

Malonmono-1 : 4 : 5-*xylidide*—1 : 4 : 5-Xylidine (15 g.). and ethyl malonate (30 g.) were heated similarly for 8 hours at 120-25° as usual and subsequently treated as the preceding compound. It was crystallised from dilute alcohol (1:6), m. p. 197°. Solubility is similar to that of the preceding compound. (Found: N, 13·57. $C_{11}H_{14}O_2N_2$ requires. N, 13 59 per cent,).

Action of bromine on acetoxyhydroxymercurimalonamide.—The mercury compound of malonamide was treated with an aqueous solution of bromine till no more bromine was absorbed. It was then heated to boiling when all the compound went in solution. The solution on cooling deposited a crystalline product which when filtered and washed with alcohol, melts at 293°. This was identical with the dibromomalonamide obtained by Freund (*Ber*; 1884, **17**, 782).

(For Table I see pages 166–167)

TABLE II.

(S=Sulphatomercuri-acetoacct).

No.	Name.	Formula.	Colour change.	M. p.	Analysis. Found.	Calc.
1a.	S-anilide	$C_{10}H_9O_6NSHg_2$	Brown at 240°	Did not melt till 300°	Hg, 59·2 SO_4,14·55	59·61p.c. 14·30
2a.	S-*o*-toluidide	$C_{11}H_{11}O_6NSHg_2$	Brown above 240°	...	SO, 14·25	14·01
3a.	S-*p*- do	$C_{11}H_{11}O_6NSHg_2$	Brown above 250°	Did not melt till 300°	SO_4,14·6	14·01
9a.	Ethyl sulphatomercuri-acetoacetate	$C_6H_8O_7SHg_2$	Yellow above 200°, reddish brown at 230°	...	SO_4,14·7	15·3
12a.	Hydroxysulphatomercuri malon-mono-phenylamide	$C_{18}H_{18}O_{10}N_4SHg_4$	Yellow above 250° Brown at 265°	...	Hg, 62·53 SO_4, 8·1	62·4 7·49
26a.	Hydroxysulphato-mercury malonamide	$C_6H_{10}O_{10}N_4SHg_4$	does not decompose till 300°	..	Hg, 70·4 SO_4, 7·9	70·8 8·49

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TABLE

(A=Acetoxyhydroxymercurimalon-.

No.	Name.	Formula.
1.	D-anilide	$C_{14}H_{15}O_6NHg_2$
2.	D-*o*-toluidide	$C_{15}H_{17}O_6NHg_2$
3.	D-*m*-toluidide	$C_{15}H_{17}O_6NHg_2$
4.	D-*p* toluidide	$C_{15}H_{17}O_6NHg_2$
5.	D-*α*-naphthylamide	$C_{18}H_{17}O_6NHg_2$
6.	D-*β*- do	$C_{18}H_{17}O_6NHg_2$
7.	D. 1 : 3 : 4-xylidide	$C_{1\text{[illegible]}}H_{19}O_6NHg_2$
8.	D-1 : 4 : 5-xylidide	$C_{1\text{[illegible]}}H_{19}O_6NHg_2$
9.	Ethyl-diacetoxymercury-acetoacetate	$C_{10}H_{14}O_7Hg_2$
10.	D-*m* nitranilide	$C_{14}H_{14}O_8N_2Hg_2$
11.	Ethyldiacetoxymercury-malonate	$C_{11}H_{16}O_8Hg_2$
12.	A-monophenylamide	$C_{11}H_{12}N_2O_5Hg_2$
13.	A-mono-*o*-toluidide	$C_{12}H_{11}O_5N_2Hg_2$
14.	A-mono-*m*-toluidide	$C_{12}H_{14}O_5N_2Hg_2$
15.	A-mono-*p*-toluidide	$C_{12}H_{14}O_5N_2Hg_2$
16.	A-mono-a-naphthylamide	$C_{15}H_{14}O_5N_2Hg_2$
17.	A-mono-*β*-naphthylamide	$C_{15}H_{14}O_5N_2Hg_2$
18.	A-mono-1 : 3-4-xylidide	$C_{13}H_{16}O_5N_2Hg_2$
19.	A-mono-1-4-5-xylidide	$C_{13}H_{16}O_5N_2Hg_2$
20.	A-amide	$C_5H_8O_5N_2Hg_2$

J.

D=diacetoxymercuriacetoacet-)

Colour changes.	M. p.	Analysis Found.	Analysis Calc.
...	204° (decomp.)	Hg, 57·26 N, 2·23	57·72 p.c. 2·02
...	184°	Hg, 56·12 N, 2·07	56·57 1·98
...	194° (decomp.)	Hg, 56·21	56·57
...	181°-82°	Hg, 56·96	56·57
...	200° (decomp.)	Hg, 53·6	53·83
...	197°	Hg, 53·4	53·83
...	192°	Hg, 55·01	55·48
...	204°	Hg, 55·00	55·48
...	does not melt till 300°	Hg, 61·7	61·9
Yellow and then reddish brown liquid at 270°	decomp. above 200°	Hg, 54·44	54·2
...	does not melt till 300° (decomp.)	Hg, 58·6	59·16
Turns yellow above 260°	,, ,, decomp. till 300°	Hg, 60·9	61·25
	decomposes above 270°	Hg, 59·91 N, 4·09	60·00 4·2
Yellow above 96° Brown at 290°	does not melt till 300°	Hg, 59·68	60·06
Reddish brown above 280°	...	Hg, 59·99	60·00
...	278° (decomp.)	Hg, 56·54	56·28
...	275° (decomp.)	Hg, 57·4	56·98
Yellow above 250°	240° (decomp.)	Hg, 58·35	58·82
Yellow above 260 & Brown at 275°	...	Hg, 59·04	58·82
...	does not melt till 300°	Hg, 69·9	69·44

CHEMISTRY DEPARTMENT,
BARODA COLLEGE, BARODA.

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XXII Mercury Acetamide as a Mercurating Agent.

BY K. G. NAIK AND L. D. SHAH.

The mercuration of organic compounds has been studied by a number of workers (Dimorth, *Ber.*, 1898, **31**, 2154; 1899, **32**, 758; 1902; **35**, 2044; Schoeller and Scrauth, *Ber.*, 1908, **41**, 2089; 1909, **42**, 778; Hoffmann, *Ber.*, 1898, **31**, 1904; 1900; **33** 1328; Petterson, *J. pr. Chem.*, 1912, **86**, 458, etc.). The most commonly employed reagents are mercuric oxide and the acetate but mercury acetamide has seldom been used for the purpose. The only isolated instance where mercury acetamide is used as a mercurating agent is its action on methylmalonate (Scholeller and Scrauth *Ber.*, 1909, **42**, 784).

From the experiments recorded herein, it appears that mercury acetamide can be employed as fruitfully as the acetate for the preparation of organomercury compounds Thus the substances enumerated below, *viz*; (1) cyanacet-methylamide, (2) cyanacet-ethylamide, (3) cyanacet-propylamide, (4) cynacet-butylamide, (5) cyanacet-*iso*butylamide, (6) cyanacet-amylamide, (7) cyanacet-*iso*hexylamide, (8) cyanacet-heptylamide, (9) ethyl cyanoacetate, (10) cyanoacetamide, (11) cyanoacetanilide, (12) cyanacet-*m*-toluidide, (13) cyanacet-*o*-toluidide, (14) cyanacet-*p*-toluidide, (15) cyanacet-benzylamide (16) cyanacet-α-naphthylamide, (17) cyanacet-βnaphthylamide, (18) cyanacet 1 : 3 : 4-xylidide, (19) cyanacet-1: 4 :5-xylidide are all attacked by mercury acetamide, one of the hydrogens of the reactive methylene group being replaced by the hydroxymercuri (—HgOH) group.

The properties of the compounds indicate the presence of a very weak C–Hg bond such as is always found when the carbon involved is in the α-position to a-CO-group. Thus they are readily decomposed by hot 0·25N hydrochloric acid. Hydrogen sulphide, ammonium sulphide or sodium sulphide causes the formation of black mercuric sulphide. Potassium iodide ruptures the C—Hg linkage with the consequent formation of alkali hydroxide. Phenylhydrazine and hydrazine hydrate are found to liberate metallic mercury.

The general constitution assigned to the above compounds follows from the considerations given below :—

1. That the mercury atom has not replaced the hydrogen atom of the aromatic nuleus because—

(*a*) Cynacet-methylamide which does not contain such a nucleus forms a similar hydroxymercuri-derivative.

(*b*) A study of the known mercury compounds shows that the nuclear mercury atom is not decomposed by dilute hydrochloric acid (0·25*N.*) (*cf.* Scrauth and Baurschmidt, *Ber.*, 1914, **47**, 2740), whereas hydroxymercuricyanacetanilide is decomposed by hot 0·25*N*-hydrochloric acid.

2. That the mercury atom has not replaced the hydrogen attached to the nitrogen atom of the —NHR group, for—

(*a*) Ethyl cyanoacetate, which does not contain such a hydrogen, forms a similar mono-mercurated product with mercury acetamide.

(*b*) The properties of the compounds suggest a carbon-mercury rather than a nitrogen-mercury linkage, because, whereas all the N—Hg compounds are decomposed by *cold* dilute acid (*cf.* Ley and Kissel, *Ber.*, 1899, **32**, 1357) the compounds described herein are decomposed by *hot* dilute acids only.

3. That the mercury atom has not entered the aliphatic part of the amido group, because—

(*a*) Cyanoacetamide which does not contain such an aliphatic part forms a similar hydroxymercuri-compound.

(4). That the mercury atom is directly attached to the carbon atom of the methylene group, for—

(*a*) Hydroxymercuricyanacet benzylamide gives monobromocyanacet-benzylamide on treatment with bromine in aqueous suspension.

(*b*) The properties and behaviour of the compounds obtained herein exactly correspond with those having mercury in the α-position to a keto or a phenyl group which renders the α-mercury atom unusually reactive.

Cyanoacetamide reacts with mercury acetamide in aqueous or alcoholic solution giving hydroxymercuricyanoacetamide, which is formulated as $CN{\cdot}CH(HgOH){\cdot}CO{\cdot}NH_2$. This constitution has been assigned to the compound on the ground that on treatment with bromine in aqueous suspension it gives dibromocyanoacetamide which is identical with the one obtained by Hesse (*J. Amer.Chem Soc.*, 1896, **18** 735) by the direct bromination of cyanoacetamide.

Petterson (*J. pr. Chem.*, 1912, *ii*, **86**, 458) obtained from mercuric acetate and ethyl cyanoacetate, hydroxymercuricyanoacetic ester, $CN{\cdot}CH(HgOH){\cdot}CO_2Et$. Probably an acetoxymercury derivative is first formed which subsequently undergoes hydrolysis under the experimental conditions. Mercury acetamide also reacts with ethyl cyanoacetate giving a quantitative yield of the hydroxymercuriderivative. In all probability an acetamido-derivative is first formed which then undergoes hydrolysis as represented below :—

$$CN{\cdot}CH_2{\cdot}CO_2Et \xrightarrow{Hg(NHAc)_2} CN{\cdot}CH(Hg{\cdot}NHAc{\cdot})Co_2Et \xrightarrow{H_2O} CN.CH(HgOH){\cdot}CO_2Et.$$

The formation of the same product from mercuric acetate and mercury acetamide naturally raises the question as to the constitution of the latter. Ley and Kissel (*Ber*, 1899, **32**, 1357) deduced from the low electrical conductivity of mercury acetamide that it contains an N—Hg bond. It is well-known that, in order that a mercuric salt may react with an aromatic organic compound it must be capable of hydrolytic dissociation. Hence it may be that during the reaction between mercury acetamide and substituted cyanoacetamides, the former may react in the tautomeric form (II) containing the O–Hg linkage.

$$\underset{\text{(I)}}{(CH_3{\cdot}CO{\cdot}NH)_2Hg} \longrightarrow \underset{\text{(II)}}{(CH_3{\cdot}\overset{\overset{\large NH}{\|}}{C}{\cdot}O)_2Hg}$$

The latter form is susceptible to hydrolytic dissociation, since all mercuric salts of oxyacids are considerably hydrolysed in aqueous solution.

EXPERIMENTAL.

The hydroxymercuri-derivatives of the substituted cyanoacetamides were prepared by the action of mercury acetamide on the cyanoacetamides in equimolecular proportion in presence of alcohol.

Hydroxymercuricyanacetmethylamide. — Cyanacetmethylamide (2 g.) dissolved in alcohol, was heated to boiling and a hot solution of mercury acetamide (6·5 g.) in alcohol was added. A snow white flocculent precipitate immediately appeared which settled down in the course of about twelve hours. The precipitate was washed with alcohol and then with distilled water several times in order to remove any unchanged reactants. The product is insoluble in most organic solvents. It begins to turn brown at 287° but does not melt till 300°. (Found : Hg, 63·98 ; N, 8·74. $C_4H_6O_2N_2Hg$ requires Hg, 63·69 ; N, 8·90 per cent.).

Action of Potassium Iodide.—0·127 G. of the above compound was suspended in water and about one g. of potassium iodide was added. The mixture was refluxed on a sand-bath for four hours and the liberated alkali was titrated against 0·0174*N*-hydrochloric acid of which 44·7 c. c. were required. This shows the presence of 1·923 equivalents of alkali indicating that the splitting of the C—Hg linkage is almost quantitative.

Action of Hydrochloric Acid.—The above mercury compound is slowly decomposed by 0·25*N*-hydrochloric acid (hot) giving the original amide and mercuric chloride.

Action of Phenylhydrazine.—About 1 g. of the mercury compound was treated with 2 c. c. of phenylhydrazine. A vigorous reaction ensued in the cold and effervescence due to liberated nitrogen was observed. A grey precipitate of metallic mercury was formed which quickly collected and settled at

the bottom of the flask. The mixture was then diluted with water and filtered. The solution on concentration and cooling deposited shining needles of pure cyanacetmethylamide, m. p. 101°.

Hydroxymercuricyanacetethylamide.—This was prepared from 1 g. of cyanacetethylamide and 2·9 g. of mercury acetamide. It does not melt till 300° but turns brown above 265°. (Found: Hg, 60·70; N, 8·76. $C_5H_8O_2N_2Hg$ requires Hg, 60·98; N, 8·54 per cent.).

*Hydroxymercuricyanacet-*n*-propylamide* was prepared from equimolecular quantities of cyanacet *n*-propylamide and mercury acetamide in presence of alcohol. It begins to turn brown above 265° and melts with decomposition at 280°. (Found: Hg, 58·24; N, 8·42. $C_6H_{10}O_2N_2Hg$ requires Hg, 58·48; N, 8·19 per cent.).

*Preparation of cyanacet-*n*-butylamide.*—In the preparation of the alkyl amides of cyanacetic ester the method of Bakes, West and Whitely (*J. Chem. Soc.*, 1921, **119**, 367) was employed. Ethyl cyanoacetate (10 g.) and *n*-butylamine (6·5 g.) were mixed up in a sealed tube which was kept for twenty-four hours and then heated at 125° for six hours. After cooling the red crystalline mass was washed with petroleum and crystallised from benzene—petroleum mixture when it separated in the form of white slender needles, m. p. 73°. It is very soluble in alcohol, chloroform, benzene, and toluene but sparingly in petroleum. (Found: N, 20·00 per cent.)

*Hydroxymercuricyanacet-*n*-butylamide.*—Prepared from cyanacet-*n*-butylamide and mercury acetamide in the usual manner, it did not undergo any change till 300°. Found: Hg, 55·88; N, 8·12. $C_7H_{12}O_2N_2Hg$ requires Hg, 56·18; N, 7·87 per cent.).

Preparation of Cyanacetisobutylamide.—Ethyl cyanoacetate ~~(10g.)~~ and *iso*butylamine (6·5 g.) were condensed in the usual way. The mixture on strong cooling solidified. It was purified by crystallisation from hot water (charcoal). It is

very soluble in all the organic solvents, and melts at 45°. (Found: N, 20·06· $C_7H_{12}ON_2$ requires N, 20·00 per cent.).

*Hydroxymercuricyanacet*iso*butylamide* turns brown above 280° but does not melt till 300°. (Found: Hg, 56·43; N, 7·72· $C_7H_{12}O_2N_2Hg$ requires Hg. 56·18; N, 7·87 per cent.).

Preparation of Cyanacet—n-*-amylamide.*—Ethyl cyanoacetate and *n*-amylamine were condensed in the usual manner. The product was crystallised from benzene-petroleum mixture after purifying it with bone charcoal. It formed feathery needles, m. p. 47°. (Fonnd: N, 18·60. $C_8H_{14}ON_2$ requires N, 18·18 per cent).

Hydroxymercuricyanacet-n-*amylamide* melts with decomposition at 285°. (Found: Hg, 54·40; N, 7 43. $C_8H_{14}O_2N_2Hg$ requires Hg, 54·06: N, 7·57 per cent.).

Preparation of Cyanacetisohexylamide.—Ethyl cyanoacetate (10g) and *iso*hexylamine (9 g,) were condensed in the usual manner. The product is very soluble in alcohol, benzene, etc. It was crystallised from water as slender, colourless needles, m, p. 42°. (Found: N, 16·92. $C_9H_{16}ON_2$ requires N, 16·66 per cent.).

*Hydroxymercuricyanacet*iso*hexylamide* melts with decomposition at 273°. (Found: Hg, 51·96; N, 7·08. $C_9H_{16}O_2N_2Hg$ requires Hg. 52 09; N, 7·29 per cent.)

Preparation of cyanacet-n-*heptylamide.*—This was prepared from ethyl cyanoacetate (10 g.) and *n*-heptylamine (10 g,) in the usual manner. It is very soluble in alcohol, acetone, ethyl acetate, and benzene and sparingly in ether and petroleum. It separates from benzene—petroleum mixture in the form of fine, colourless needles melting at 67°. (Found: N, 15·20. $C_{10}H_{18}ON_2$ requires N, 15 38 per cent.).

Hydroxymercuricyanacet-n-*heptylamide* was prepared as usual from cyanacet-*n*-heptylamide and mercury acetamide. It turns brown at 270° and melts at 284°. (Found: Hg, 49·51; N 6·99. $C_{10}H_{18}O_2N_2Hg$ requires Hg, 50·25; N, 7·04 per cent.).

Ethyl Hydroxymercuricyanoacetate.—Ethyl cyanoacetate was treated with the calculated quantity of mercury acetamide in alcoholic solution. The product is insoluble in most of the ordinary organic solvents and does not suffer any change till 300°. (Found: Hg, 61·08; N, 4·37. $C_5H_7O_3NHg$ requires Hg, 60·79; N, 4·25 per cent.).

Action of potassium Iodide.—0·1484 G. of ethyl hydroxy-mercuri-cyanoacetate was suspended in water and about 1 g. of potassium iodide was added. The mixture was refluxed for four hours and the liberated alkali was titrated against 0·0174*N*-hydrochloric acid (50·9 c. c.). This shows the presence of 1·96 equivalents of alkali, indicating the complete rupture of the C—Hg linkage.

Hydroxymercuricyanoacetamide was prepared from equimolecular quantities of cyanoacetamide and mercury acetamide in aqueous solution. It does not melt till 300°. (Found: Hg, 66·24; N, 9·70. $C_3H_4O_2N_2Hg$ requires Hg, 66·66; N, 9·33 per cent.).

Action of Bromine.—Aqueous bromine was slowly added to a suspension of the above compound in water, till it was no longer absorbed. The flask was finally heated on a water-bath for about half an hour. The solution was evaporated to dryness and the residue was extracted with benzene. On cooling the benzene extract, small needles separated out which, on recrystallisation from alcohol melted at 126°. It is identical with dibromocyanoacetamide.

The mercury derivatives of the substituted cyanoacetamides containing aromatic nuclei were similarly prepared by mixing equimolecular quantities of the amides and mercury acetamide in hot alcoholic solution.

Hydroxymercuricyanacetanilide does not undergo any change till 300°. (Found: Hg, 53·48; N, 7·22 $C_9H_8O_2N_2Hg$ requires Hg, 53·19; N, 7·45 per cent.).

Action of Hydrochloric Acid.—The above compound was treated with 25 c. c. of 0·25*N*-hydrochloric acid. On heating,

a clear solution was obtained which on cooling deposited small needles which were collected and on purification proved to be cyanacetanilide, m. p. 199°.

Hydroxymercuricyanacet-m-toluidide does not undergo any change till 300°. (Found : Hg, 51·70; N, 7·23. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28; N, 7·18 per cent.).

Hydroxymercuricyanacet-o-toluidide does not melt below 300°. (Found : Hg, 50·94. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 per cent.).

Hydroxymercuricyanacet-p-toluidide does not melt till 300°. (Found : Hg, 50·90. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 per cent.).

Hydroxymercuricyanacetbenzylamide melts with decomposition at 293°. (Found : Hg, 55·98. $C_{10}H_{10}O_2N_2Hg$ requires Hg, 51·28 percent.).

Action of Bromine.—The above compound was treated with bromine till it was no longer absorbed. The flask was heated on a water-bath for about 15 mins. when a clear solution was obtained. On cooling, the solution deposited light, white tufts, which after recrystallisation from benzene melted at 92°. (Found : Br, 31·44· $C_{10}H_{10}ON_2Br$ requires Br, 31·62 per cent.).

Reduction of the Bromo-derivative.–0·138 G. of the substance liberated iodine equivalen to 54·6 c.c. of 0·02N-sodium thiosulphate. (Found ; Br, 31·65. Calc. Br (labile), 31·62 per cent).

Hydroxymercuricyancet-α-naphthylamide turns grey at 253° and melts with decomposition at 272°. (Found : Hg, 47·23. $C_{13}H_{10}O_2N_2Hg$ requires Hg, 46·95 per cent.).

Hydroxymercuricyanacet-β-naphthylamide melts with decomposition at 283°. (Found ; Hg, 46·71. $C_{13}H_{10}O_2N_2Hg$ requires Hg, 46 95 per cent.).

Hydroxymercuricyanacet-1 : 3 : 4-*xylidide* does not melt till 300°. (Found : Hg, 50 00. $C_{11}H_{12}O_2N_2Hg$ requires Hg, 49·51 per cent.).

Hydroxymercuricyanacet 1 : 4 : 5-*xylidide* does not undergo any change till 300°. (Found : Hg, 49·87. $C_{11}H_{12}O_2N_2Hg$ requires Hg, 49·51 per cent.).

The authors take this opportunity to express their gratitude to the Government of His Highness the Gaekwar of Baroda for a grant which has defrayed the expenses incurred in this work.

Chemistry Department
The College, Baroda.

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XXIII The Formation of the Sodium Derivatives of Compounds Containing a Reactive Methylene Group.

By K. G. Naik and L. D. Shah.

It is well-known that the hydrogen atoms in groupings such as $-CO-CH_2-CO-$ $\equiv C-CH_2-C\equiv$

$-CO-NH-CO-$ $H{\cdot}C\equiv$ $HO{\cdot}C=$

are replaceable by sodium, and that the property depends upon the accumulation of residual affinity in the immediate neighbourhood of the replaceable hydrogen. Bland and Thrope (*J. Chem. Soc.*, 1912, **101**, 874) have advocated that the stability of the sodium compounds of the various glutaconic esters must be dependent upon the acid character of the displaced hydrogen, the acidity being determined by the nature of the groups attached to the carbon atom which carries the hydrogen atom and they further hold that in those cases in which one carbethoxy group is attached to the carbon atom, the sodium compound is completely dissociated by water. It is also known that ethyl cyanoacetate and cyanoacetamide give mono-sodium derivatives (Henry, *Comp. rend.*, 1887, **104**, 1619; Hesse, *Amer. Chem. J.*, 1896, **18**, 724). The present work was therefore undertaken to study the relationship which may exist between the acid character of the hydrogen atom of a reactive methylene group and the formation of its sodium derivative by the replacement of such a hydrogen. The following substances were examined :

(1) Cyanacet-*m*-toluidide, (2) cyanacet-*o*-toluidide, (3) cyanacet-*p*-toluidide, (4) cyanacetbenzylamide, (5) cyanacet-α-naphthylamide, (6) cyanacet-β-naphthylamide, (7) cyanacet-

methylamide. (8) cyanacetbutylamide and (9) cyanacetheptylamide.

All the substances enumerated above react with metallic sodium in presence of dry benzene or anhydrous ether, yielding products having the general formula, CN·CHNa·COR (R=OEt, NH_2, NHMe, etc.).

The above general constitution has been assigned to the compounds from the following considerations :

(1) That the sodium atom has not replaced the hydrogen atom of the nucleus, for, cyanacetmethylamide which does not contain such a nucleus forms a similar mono-sodium derivative.

(2) That the sodium atom has not entered the aliphatic part of the amido group, for, cyanoacetamide which does not contain such an aliphatic part, forms a similar mono-substitution product with metallic sodium (Hesse, *loc. cit.*).

(3) That the sodium atom has not replaced the hydrogen attached to the nitogen atom of the — NH·R group for,

(*a*) Ethyl cyanoacetate, which does not contain such a hydrogen forms a similar mono-substituted product with metallic sodium (Henry, *loc. cit.*).

Sidgwick and Baewer (J. *Chem*. *Soc.*, 1925, **127**, 2379) have shown that the alkaline derivatives of β-diketones, β-ketonic esters, *o*-hydroxy aromatic esters and aldehydes and *o*-nitrophenols behave in one of the three ways as exemplified below :

(I) The sodium derivative of ethyl malonate is insoluble in benzene and chars without melting : it behaves as a salt.

(II) The sodium derivative of ethyl methylmalonate dissolves in benzene to form a clear solution from which the compound does not separate immediately even on concentration; but once it has separated, it is quite insoluble in benzene or toluene.

(III) The sodium derivative of ethyl acetoacetate is soluble in hot toluene and melts to a clear liquid at 108°.

The compounds obtained during the present course of the work must be classed as salts of type I given above, since they

are insoluble in benzene and toluene and do not give definite melting points.

During the course of their investigations on the factors governing the reactivity of the hydrogen atoms of a reactive methylene group situated between two negative groups as in the case of compounds containing the groupings.

$$-CO\cdot CH_2\cdot CO- \quad \text{and} \quad CN\cdot CH_2\cdot CO-,$$

it has been observed by Naik and his collaborators (*J. Chem. Soc.*, 1921, **119**, 379 ; 1922, **121**, 2592, etc.) that the reactivity increases in direct proportion to the increase in the negativity of the carbonyl group with its attached groupings ; so that in a series like—

(1) $CH_2(CO\cdot NH_2)_2$ (2) $NH_2\cdot CO\cdot CH_2\cdot CO\cdot NHR$
(3) $CH_2(CO\cdot NHR)_2$ (4) $EtO\cdot CO\cdot CH_2CO\cdot NHR$
(5) $CN\cdot CH_2CO_2Et$ (6) $CH_2(CO_2Et)_2$

the reactivity increases from (1) to (6).

The experiments described herein afford clear evidence that the interaction of metallic sodium with compounds containing the methylene radicle, depends on the electronegative character of the attached groups. Thus, ethyl cyanoacetate reacts with metallic sodium with the greatest rapidity forming the monosubstitution product even in the cold, while cyanacet-*m*-toluidide required about six hours' heating in benzene solution. In the case of cyanacet-α-naphthylamide the reaction is found to be still slower.

EXPERIMENTAL

Sodiocyanacet-m-*toluidide.*—To a flask containing molecular sodium (0·3 g.) (prepared by heating under boiling toluene in the usual way) about 30 c. c. of anhydrous benzene were added, followed by cyanacet-*m*-toluidide (2 g.). The flask was heated under reflux when the amide went into solution. After about half an hour, a white gelatinous mass began to separate. The heating was continued for six hours and the mixture filtered hot. The solid obtained was washed with hot benzene several times and then with light petroleum (b. p. 50-60°). It was then dried in a desiccator over sulphuric acid.

The product was a white amorphous mass insoluble in most of the ordinary organic solvents such as benzene, ether and petroleum. It charred at 230° but did not melt even up to 300°. Even when preserved in a sealed tube, the product turned pink. (Found: Na, 11·88; N, 13·89. $C_{10}H_9ON_2Na$ requires Na, 11·73; N, 14·28 per cent.).

Action of Hydrochloric Acid.—About 0·5 g. of the above substance was treated with 5 c. c. of concentrated hydrochloric acid. The substance underwent decomposition which was evident from the profound frothing that took place. Water was then added to the mixture and the solid was washed several times with cold water. It was then crystallised from benzene and identified as pure cyanacet-*m*-toluidide, m. p. 132°.

Action of Water.—0·124 G. of the above substance suspended in water was heated for about half an hour. The liberated alkali was titrated against 0·051 *N*-hydrochloric acid of which 12·6 c. c. were required. This showed the presence of 1·02 equivalents of alkali indicating that the decomposition was quantitative.

Sodiocyanacet-o-toluidide was prepared as in the above case. It has no definite melting point but turned deep red above 190° and blackened at 220 without melting. (Found: Na, 11·94; N, 14·45. $C_{10}H_9ON_2Na$ requires Na, 11·73; N, 14·28 per cent.).

Sodiocyanacet-p-toluidide.—The reaction was found to be much slower in this case and took nearly twelve hours for completion. The compound turned deep red above 245° and then blackened without melting to a clear liquid. (Found: Na, 11·58. $C_{10}H_9ON_2Na$ requires Na, 11·73 per cent.).

Sodiocyanacetbenzylamide was prepared from cyanacetbenzylamide (2 g.) and metallic sodium. It changed its colour from white to pink. It was insoluble in benzene and toluene and blackened at 205° without melting. (Found: Na, 12·05. $C_{10}H_9ON_2Na$ requires Na, 11·73 per cent.).

Sodiocyanacet-α-naphthylamide was prepared from cyanacet-α-naphthylamide (2 g.) and metallic sodium (0·3 g) in pre-

sence of anhydrous benzene. The heating had to be continued for twelve hours. The compound turned deep red above 170° and at high temperatures fused to a dark mass without melting (Found : Na, 9·82. $C_{13}H_9ON_2Na$ requires Na, 9·91 per cent.).

Sodiocyanacet-β-naphthylamide was prepared as in the above case from cyanacet-β naphthylamide and metallic sodium. It turned brown above 205° but did not melt even up to 300°. (Found : Na, 9·78. $C_{13}H_9ON_2Na$, requires Na, 9·91 per cent.).

Sodiocyanacetmethylamide.—In the case of the alkyl amides of cyanoacetic acid, ether was used as the solvent.

Cyanacetmethylamide (2 g.) was put in a flask and covered with about 25 c. c. of dry ether distilled over sodium. Finely divided sodium (0·4 g.) which had been purified by boiling under toluene, was then added. A calcium chloride tube was attached to the flask. At the end of two days the precipitated solid was taken out and extracted with small portions of hot benzene and finally washed with light petroleum. On drying in a desiccator over sulphuric acid, the product assumed a pink colour. It turned deep red above 190° and melted with decomposition at 225°. (Found : Na, 19·42. $C_4H_5ON_2Na$ requires Na, 19·17 per cent.).

Sodiocyanacetbutylamide was prepared as in the preceding case. The reaction was found to be much rapid in this case. The product melted with decomposition at 200°. (Found : Na, 14·03; N, 17·37. $C_7H_{11}ON_2Na$ requires Na, 14·20; N, 17·28 per cent.)

Sodiocyanacetheptylamide.—This was prepared as in the preceding cases by the action of metallic sodium on cyanacetheptylamide in presence of anhydrous ether. A red solid was obtained which was repeatedly extracted withhot benzene and finally washed with light petroleum. It melted with decomposition at 195°. (Found: Na, 11·9. $C_{10}H_{17}ON_2Na$ requires Na, 11·27 per cent.).

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CHEMISTRY DEPARTMENT,
BARODA COLLEGE, BARODA.

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XXIV Interaction of Sulphuryl Chloride with Substances Containing the Reactive Methylene Group. Part II.

By K. G. NAIK AND N. T. TALATI.

The present communication is a continuation of the work done by Naik and Shah (*J. Indian Chem. Soc.*, 1927, **4**, 11).

The main results of the interaction of sulphuryl chloride with various amides and substituted amides of malonic and methyl malonic acids, obtained herein, can be summarised as under:—

I. (*a*) Conversion of the group $:CH_2$ into $:CCl_2$ or (*b*) of the group :CHMe into :CClMe by complete replacement of the methylene hydrogen atom or atoms by chlorine without chlorination of the nucleus:—Malon-di-*m*-nitranilide, malon-di-*p*-nitranilide, malon-di-*o*-nitranilide, malon-diethylamide, malon-di-*iso*butylamide, malon diheptylamide, malon-di 1:4:5 xylidide, and malonamide undergo this change under (*a*) whereas methylmalon-diethylamide, methyl-malon-di-*iso*-butylamide, and methylmalon-dibenzylamide undergo this change under (*b*).

Further it was found that the same type of reactivity persisted oven among the aliphatic amides of the methyl-malonic acid. It may be noted here that in these compounds, one of the hydrogen atoms of the methylene group is replaced by the methyl group. Thus methylmalon-diethylamide, on interaction with sulphuryl chloride, yields a monochloro-derivative:—

$$(EtNH{\cdot}CO)_2CH{\cdot}Me + SO_2Cl_2 = (EtNH{\cdot}CO)_2CCl{\cdot}Me + HCl + SO_2$$

II. Conversion of the group $:CH_2$ into :CHCl without chlorination of the nucleus :—Malon-tetraphenylamide undergoes this change.

Type I. Malon-di-*m*-nitranilide reacts with sulphuryl chloride as under :—

$$(NO_2{\cdot}C_6H_4{\cdot}NH{\cdot}CO)_2CH_2 + 2SO_2Cl_2 = NO_2C_6H_4{\cdot}NH{\cdot}CO)_2CCl_2 + 2HCl + 2SO_2.$$

The fact that the substance produced from malon-di-*m*-nitranilide has this constitution, is based on arguments similar to those advanced by Naik and Shah (*loc. cit.*).

It may, however, be pointed out that malontetraphenylamide, where there is no hydrogen atom attached to the nitrogen, yields a monochloro-derivative. These go to prove that sulphuryl chloride reacts at the methylene group.

Type II. The interaction of malontetraphenylamide with sulphuryl chloride as stated above follows a different course, yielding, a monochloro-compound:-

$$[Ph_2N\,CO]_2CH_2 + SO_2Cl_2 = [Ph_2N{\cdot}CO]_2CHCl + HCl + SO_2.$$

In this case, inspite of the two hydrogen atoms of the methylene group being available, only one is attacked. This course of the reaction is not an abnormal one, as is evident from the work of Naik (*J. Chem. Soc.*, 1921, **119**, 38?), Naik and Shah (*loc. cit.*) and West (*J. Chem Soc.*, 1922, **121**, 2196).

The experiments described here afford clear evidence. with regard to the reactivity towards sulphuryl chloride of compounds containing the reactive methylene group, that it depends on the electronegative character of the adjoining groups. For example, sulphuryl chloride reacts more vigorously with malon-dinitranilide than with malonamide, while the reaction with ethyl malonate is the most vigorous, taking place at the ordinary temperature. So in a series like:-

(I) $CH_2(CO{\cdot}NH_2)_2$

(II) $CH_2(CO{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2)_2$

(III) $CH_2(CO_2Et)_2$

the reactivity which is less pronounced in (I) becomes more and more manifest with increasing negativecharacter of the adjoining groups.

EXPERIMENTAL.

*Preparation of Malon-di-*m- *and* -p *nitranilides.*—These

amides were prepared by condensing ethyl malonate and the corresponding nitraniline in equimolecular proportions, on the basis of the preparation of malonamide by Whiteley (*J. Chem. Soc.*, 1903, **83**, 36). The solid obtained was extracted with alcohol and finally crystallised from acetic acid in granulated mass. The *m*-compound had m. p. 196°, whereas the *p*-compound – a faintly yellowish crystalline one – had m. p. 243°.

Preparation of Malon-di-o-nitranilide.—The reaction with ethyl malonate and *o*-nitraniline did not go even at 200°. Hence the amide was prepared from malonic acid and *o*-nitraniline using phosphorus oxychloride as a condensing agent as used by Backes, West and Whiteley (*J. Chem. Soc.* 1921, **119**, 371). The amide was extracted with benzene in which it is soluble. It was crystallised from alcohol as yellowish, glistening, feathery needles, m. p. 182°. All the three malon-nitranilides were soluble in alcohol, acetic acid, benzene and toluene; sparingly so in carbon tetrachloride, chloroform, nitrobenzene, ethyl acetate but insoluble in ether, carbon disulphide and light petroleum. [Found: N, 16·41 (*ortho*), 16·48 (*meta*), 16·13 (*para*). $C_{15}H_{12}N_4O_5$ requires N, 16·28 per cent.].

Dichloromalon-di-nitranilide.—Malon-di-*m*-nitranilide (1 g.) and sulphuryl chloride (1 g.) were made to react by the method followed in the preparation of dichloromalon-diphenylamide (Naik and Shah, *loc. cit.*). The product obtained was crystallised from alcohol in grey leaflets, m. p. 166°.

It is fairly soluble in alcohol, acetic acid, benzene, and toluene; fairly so in nitrobenzene, carbon tetrachloride and ethyl acetate, but almost insoluble in ether, carbon disulphide and light petroleum. (Found: Cl, 17·31. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 7·19 per cent.).

*Dichloromalon-di-*p*-nitranilide.*—The above compound was obtained as yellow crystalline mass when malon-di-*p* nitranilide (1 g.) was treated with sulphuryl chloride (1 g.) in the presence of 50 c. c. of benzene in the usual way. It was crystallised from alcohol in yellowish needles, m. p. 178°. It behaves in

almost the same way with different organic solvents, as the previous one does. (Found : Cl, 17·35. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 17·19 per cent.).

Dichloromalon-di-o-nitranilide.—It was prepared from malon di-*o*-nitranilide (1 g.) and sulphuryl chloride (1 g.) in the presence of dry benzene in the usual way. The solid product was crystallised from alcohol in yellowish prisms, m. p. 152°. The solubility of this compound is of the same order as that of the previous ones. (Found : Cl, 17·61. $C_{15}H_{10}O_6N_4Cl_2$ requires Cl, 17·19 per cent.).

Dichloromalon-diethylamide.—On treating malon-diethylamide (1 g.) with sulphuryl chloride (1 g.) in the usual way, white mass was deposited on standing. The resulting product was crystallised from alcohol in the form of white needles, m. p. 131°. The product has a solubility of the same order as that of the compound above described. (Found : Cl, 31·30. $C_7H_{12}O_2N_2Cl_2$ requires Cl, 30·28 per cent.).

Dichloromalon-di-isobutylamide.—This compound was prepared from malon-di-*iso*butylamide (1 g.) and sulphuryl chloride (1 4 g.) in the same way as the preceding chloride. After the reaction was over, the product crystallised from water in the form of white needles, m.p. 84°. It is soluble in almost all organic solvents except light petroleum. (Found : Cl, 25·19. $C_{12}H_{20}O_2N_2Cl_2$ requires Cl, 25·?9 per cent.).

Dichloromalon-diheptylamide.—Malon-diheptylamide (1 g.) and sulphuryl chloride (1 g.) were made to react in the usual way described. The mass on crystallisation from benzene gave colourless prismatic needles, m. p. 96°. It is found to be identical with the dichloromalon-diheptylamide prepared by Naik and Trivedi (*J. Indian Chem. Soc.*, 1930, **7**, 246) by condensation of the amide with selenium tetrachloride.

Dichloromalon-di(1 : 4 : 5) *xylidide.*—The above compound was obtained as a colourless crystalline mass, when malon-di-(1 : 4 : 5) xylidide (2 g.) and sulphuryl chloride (2 g.) were treated in the usual way. It was crystallised from alcohol in

colourless needles, m.p. 170°. It is found to be identical with dichloromalon-di-(1 : 4 : 5) xylidide prepared by Naik and Trivedi (*loc. cit.*)

Dichloromalonamide.—As under the above conditions the malonamide was inactive, it was directly treated with sulphuryl chloride. The reaction started slowly on heating, with an evolution of sulphur dioxide and hydrogen chloride. When the reaction slackened after three hours, the liquid was diluted with acetic acid and filtered hot. The filtrate on standing gave colourless, shining needles. They were washed with dry petroleum and crystallised from glacial acetic acid, m. p. 203° It is found to be identical with dichloromalonamide prepared by Zincke and Kegel (*Ber.*, 1890, **23**, 245).

Monochloromalon-tetraphenylamide.- Malontetraphenylamide (1 g.) and sulphuryl chloride (0·5 g) were made to react as usual. The filtrate on leaving overnight deposited colourless crystals, which were recrystallised from benzene, m. p. 204°. It is found to be identical with monochloromalon-tetraphenylamide prepared by West (*J. Chem. Soc.* 1922, **121**, 2200) by direct chlorination of the amide.

Preparation of Methylmalon-diethylamide.—The amide was prepared from methylmalonic ester and ethylamine by the method of Backes, West and Whiteley (*loc. cit.*, p. 366) adopted for the preparation of malon-diethylamide. The mass was crystallised from benzene in colourless needles, m. p. 151°.

It is fairly soluble in almost all organic solvents and also in water, but insoluble in light petroleum. (Found : N, 16·53. $C_8H_{16}O_2N_2$ requires N, 16-28 per cent.).

Monochloromethylmalon-diethylamide.—This compound was prepared by treating methylmalon-diethylamide (1 g.) with sulphuryl chloride (1 g .) in the usual way. Colourless needles were obtained on standing for a day. It was crystallised from alcohol, m. p. 108°. Its solubility in different organic solvents closely resembles that of dichloromalon-diethylamide. (Found: Cl, 17·61. $C_8H_{15}O_2N_2Cl$ requires Cl, 17·15 per cent.)

Preparation of methylmalon-di-isobutylamide.—This amide is prepared from methylmalonic ester (10 g.) and *iso*butylamine (9 g.) by the method adopted by Backes, West and Whiteley (*loc. cit.*) for the preparation of malon *n*-propylamide. The mass was removed from the tube by dissolving in benzene. This solution on concentration gave white mass, which when crystallised from alcohol gave colourless needles, m. p. 133°. Its solubility is of the same order as that of the preceding compound. (Found : N, 12.64. $C_{12}H_{24}O_2N_2$ requires N, 12.28 per cent.).

Monochloromethylmalon-di-isobutylamide.—Methylmalon-di-*iso*butylamide (1 g.) and sulphuryl chloride (1 g.) were made to react in the usual way. The liquid on standing overnight gave white mass, which when crystallised from alcohol yielded colourless needles, m. p. 102°. It closely resembles the preceding compound, in its solubility. (Found : Cl, 13.79. $C_{12}H_{23}N_2O_2Cl$ requires Cl, 13.52 per cent.).

Monochloromethylmalon-dibenzylamide.—This compound was prepared from methylmalondibenzylamide (2 g.) and sulphuryl chloride (2 g.). in the usual way. The product, when crystallised from benzene, gave shining pearly plates, m. p, 159°. It is soluble in chloroform and other organic solvents, like the above enumerated compound but is insoluble in light petroleum ether and water. (Found : Cl, 11.13. $C_{18}H_{19}O_2N_2Cl$ requires Cl, 10.74 per cent).

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CHEMISTRY DEPARTMENT
THE COLLEGE, BARODA.

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XXV A Study of the Interaction between Thionyl Chloride and Substances containing the Reactive Methylene ($-CH_2-$) Group. Part III.

BY K. G. NAIK AND V. B. THOSAR.

The present work is a direct continuation of a previous work (Naik and Parekh, *J. Indian Chem. Soc.*, 1930, 7, 137) the amides used being the substituted amides of acetoacetic acid and acetone dicarboxylic acid. The aim of this work is to show that the reactivity of the hydrogen atoms of the reactive methylene ($-CH_2-$) group, situated between two carbonyl groups, with respect to thionyl chloride, is in complete accordance with the hypothesis put forward (Naik, *J. Chem. Soc*, 1921, **119**, 1166, 1231; Naik and Avasare, *J. Chem. Soc*, 1922, **121**, 2592), *viz.*, that the interaction of sulphur monochloride and a compound containing a reactive methylene group, depends upon the nature of the groups attached to the two remaining valencies of the carbon atom.

Thionyl chloride was made to react with following amides in presence of dry benzene.

(1) Acetoacetanilide, (2) acetoacet-α-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet-*p*-toluidide. (5) acetoacet-α-naphthyl amide, (6) acetoacet-β-naphthylamide, (7) acetoacet-(1 : 3 : 4)-xylidide, (8) acetoacet (1 : 4 : 5)-xylidide, (9) acetone dicarboxyanilide, (10) acetone dicarboxy *o* toluidide, (11) acetone dicarboxy-*p*-toluidide, (12) acetone dicarboxy-α-naphthylamide and (13 acetone dicarboxy-β-naphthylamide.

When the solution was reflux d there was a copious evolution of hydrochloric acid with a change in the colour of the solution. The reaction was complete at the end of one hour.

The preparation of the substituted amides of acetoacetic acid was first attempted following the method described by Knorr (*Annalen*, 1886, **236**, 75) which was subsequently discarded, yield being found extremely unsatisfactory. After some trials, the method used by Ewins and King (*J. Chem.*

Soc., 1913, **103**, 104) with some modifications was found to yield satisfactory results. For the preparation of the substituted amides of acetone dicarboxylic acid, the method described by Besthorn and Garben (*Ber.*, 1900, **33**, 3439) was adopted, Amides (5 to 8) and (12 to 13) have been prepared for the first time.

The reaction in the case of substituted amides of acetoacetic acid (1 to 8) can be represented thus:

$$\left.\begin{matrix}CH_3CO\\ R\cdot NH\cdot CO\end{matrix}\right> CH_2 + SOCl_2 \rightarrow \left.\begin{matrix}CH_3CO\\ R\cdot NH\cdot C\cdot O\end{matrix}\right> C{:}S{:}O + 2HCl$$

In the case of the substituted amides of acetone dicarboxylic acid (9 to 13), although more than two molecules of thionyl chloride were taken for every molecule of the substituted amide to give ample opportunity for the substitution of sulphoxide groups for all the hydrogen atoms in the two reactive methylene groups, reaction did not proceed to this extent and the product contained only one sulphoxide group, one hydrogen atom of each methylene group having been substituted,

$$\begin{matrix}R\cdot NH\cdot CO\diagdown CH_2\\ \diagup\\ CO\\ \diagdown\\ R\cdot NH\cdot CO\diagup CH_2\end{matrix} + SOC_2 \rightarrow \begin{matrix}R\cdot NH\cdot CO\diagdown CH\\ \diagup\\ CO\\ \diagdown\\ R\cdot NH\cdot CO\diagup CH\end{matrix}\!\!\left.\begin{matrix}\\ \\ \end{matrix}\right> S{:}O + 2HCl$$

(II)

The above constitution of the sulphur compounds follows from the following considerations :

(*i*) That the two hydrogen atoms are not supplied by the phenyl group follows from the reasons, (*a*) malondimethyl amide which does not contain such a phenyl nucleus reacts similarly with thionyl chloride to give a similar sulphoxide (Naik and Parekh, *loc cit.*); (*b*) acetone dicarboxyanilide which contains two such phenyl groups also gives the same type of compound. On the supposition that the phenyl group is reactive, such a compound cannot be expected.

(*ii*) That the two hydrogen atoms are not those which are originally attached to the nitrogen atom of the -NH·R group for, (*a*) in the first place there is only one such hydrogen in a molecule of acetoacetanilide, while two hydrogen atoms have taken part in the reaction from the same molecule of acetoacetanilide; (*b*) a tertiary amide like malondimethylamide which does not contain such amido hydrogen, reacts under similar conditions with thionyl chloride to give a similar compound (Naik and Parekh, *loc cit.*).

Now taking into considerations the three compounds (*i*) $CH_3CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}R$, (*ii*) $R{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}R$ and (*iii*) $R{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}R$ it will be seen that the total negativity of the carbonyl groups with their attached radicles in the case of (*i*) is due to two groups, one of which CO·NH·R is common to all the three compounds and the other, the acetyl group, which is more negative than the partly neutralized group, CO·NH·R which is present in (*ii*) and (*iii*). Again, the negative effect of the central carbonyl group in (*iii*) is divided between two adjacent methylene groups, so that the total negative effect on each of the methylene group is smaller than that on a single methylene group when linked as $-CO{\cdot}CH_2{\cdot}CO{\cdot}$ as in (*i*) or (*ii*). Hence it was expected that the two methylene groups in (*iii*) would be less reactive than the one in (*ii*), which in its turn would be less reactive than that in (*i*). From the facts stated above, it will be quite evident that such has actually been found to be the case. Whereas compounds of the type (*iii*) have given rise to sulphoxides of the type (II), compounds of the type (*ii*) and (*i*) reacted thus :

$$\begin{matrix} R{\cdot}NH{\cdot}CO \\ R'{\cdot}CO \end{matrix}\!\!>\!CH_2 + SOCl_2 \longrightarrow \begin{matrix} R{\cdot}NH{\cdot}CO \\ R'{\cdot}CO \end{matrix}\!\!>\!C{:}S{:}O + 2HCl$$

where R' is—CH_3 or—NH·R group. Reaction in the case of (*i*) however is much faster than in case (*ii*). Such behaviour is quite in accordance with the theory, already referred to above.

As compared with the sulphoxides of the substituted amides of malonic acid, these sulphoxides are not degraded into sulphides by boiling in benzene solution in presence of a

catalyst like thionyl chloride, hydrochloric acid gas or iodine. They are also more stable towards moisture.

EXPERIMENTAL.

Acetoacet-∝-naphthylamide—Acetoacetic ester (13g.) was mixed with ∝-naphthylamine (14 g.) in a conical flask with an air condenser, and the mixture was heated quickly to boiling and kept gently boiling for 1½ minutes. On cooling, the amide crystallised out. It was filtered and washed with a mixture of benzene and light petroleum (1 :1) till it was free from the ester and the amine. It was then redissolved in hot benzene and filtered from the insoluble residue of the diamide which was also formed in the course of reaction. The filtrate was diluted with an equal volume of light petroleum (b. p. 50°-60°) and allowed to cool. Acetoacet-∝-napthylamide crystallised out in pale red small needles, m. p. 108 09°. It is highly soluble in ethyl alcohol, methyl alcoh l, benzene and nearly insoluble in light petroleum. (Found: N, 6·12. $C_{14}H_{13}O_2N$ requires N, 6·16 per cent.).

Rest of the substituted amides of acetoacetic acid (5 to 8) were similarly prepared by condensing the respective amines with ethyl acetoacetate. The results are tabulated in Table I.

Acetone dicarboxy-∝-naphthylamide.—Acetone dicarboxylic ester (10 g) and ∝-naphthylamine (11 g.) were mixed together and heated in a sealed tube at 130° for 24 hours. The reaction mixture was diluted with about 500 c. c. of benzene when the amide separated out. It was filtered and washed with benzene till free from ester and finally with ether to remove amine. It was then recrystallised from hot alcohol as pale red granular mass m. p. 165°. It is fairly soluble in glacial acetic acid, sparingly so in alcohol but insoluble in benzene, toluene, light petroleum or ether. (Found: N, 6·94. $C_{25}H_{20}O_3N_2$ requires N, 7·07 per cent.).

Acetone dicarboxy β-naphthylamide was similarly prepared from acetone dicarboxylic ester and β-naphthylamine. The results are tabulated in Table II.

Acetoacetanilide sulphoxide.—Pure dry acetoacetanilide (1·7 g.) was made to react with thionyl chloride (1·4 g.) in presence of dry benzene (30 c.c.). After refluxing for 1 hour, when the evolution of hydrochloric acid had nearly ceased, the clear solution obtained was concentrated and allowed to cool. Nothing separated out. Hence it was slowly added to a large amount of dry light petroleum (b.p. 40-60°) when a beautiful snuff coloured compound separated out. It was redissolved in benzene and separated by slow addition of light petroleum. It was then kept in an alkali desiccator till it was free from hydrochloric acid. It melts with decomposition to a thick black liquid at 90°, with a previous shrinking at 69°. (Found: N, 6·43; S, 14·26. $C_{10}H_9O_2NS$ requires N, 6·27; S, 14·35 per cent.)

All other sulphoxides were similarly prepared by treating the respective amides (1 mol.) with thionyl chloride (1 mol.) under similar conditions. The results are tabulated in Table III.

TABLE I.

New Substituted Amides of Acetoacetic Acid.

Name.	Formula.	Appearance.	Duration of heating.	M. p.	Analysis. Found.	Analysis. Calc.
Acetoacet-α naphthylamide	$C_{14}H_{13}O_2N$	Pale red short needles.	1½ min.	1[illegible]8·109°	N,6·12	6·16 p.c.
Acetoacet-β naphthylamide	$C_{1[illegible]}H_{13}O_2N$	White crystals.	1¼	103·104°	N,6·57	6·16
Acetoacet-(1 :3 :4)-xylidide	$C_{12}H_{1[illegible]}O_2N$	White short needles.	1½	92°	N,7·12	6·82
Acetoacet-(1 :4 :5)-xylidide	$C_{12}H_{15}O_2N$	Shining white tufts.	1½	96°	N,6·95	6·82

TABLE II.

New Substituted Amides of Acetone dicarboxylic Acid.

Acetone dicarboxy-α-naphthylamide	$C_{25}H_{20}O_3N_2$	Pale red granular mass.	24 hrs.	165°	N,6·94	7·07
Acetone dicarboxy-β-naphthylamide	$C_{25}H_{20}O_3N_2$	White needles.	24	207°	N,6·71	7·07

TABLE III.

Condensation Products of Thionyl Chloride with Substituted Amides of Acetoacetic and Acetone dicarboxylic Acids.

(S=Sulphoxide).

Name.	Forn u'a.	Appearance.	Shrinks at.	M P. (with decomp.)	Analysis. Found	Calc.
Acetoacetanilide-S	$C_{10}H_9O_3NS$	Snuff colour	69°	90°	S, 14·26	14·35 p c.
					N, 6 43	6·27
Acetoacet-*o*-toluidide-S	$C_{11}H_{11}O_3NS$	Pale brown	87°	110°	S, 13·79	13·50
					N, 5·94	5.90
Acetoacet-*m*-toluidide-S	$C_{11}H_{11}O_3NS$	,,	78°	93·94°	S, 13·70	13 50
Acetoacet-*p*-toluidide-S	$C_{11}H_{11}O_3NS$	Deep brown	87°	92· 3°	S, 13·17	13·50
Acetoacet-α-naphthylamide-S	$C_{14}H_{11}O_3NS$	Pale brown	92°	112°	S, 11·34	11·72
Acetoacet-β-naphthylamide-S	$C_{14}H_{11}O_3NS$	,,	82°	107°	S, 11·26	11·72
Acetoacet-(1 :3 :4)-xylidide-S	$C_{12}H_{13}O_3NS$	,,	90°	102°	S, 12·83	12·75
Acetoacet-(1 :4 :5)-xylidide-S	$C_{12}H_{13}O_3NS$	Deep brown	97°	114°	S, 13 10	12·75
Acetone dicarboxyanilide-S	$C_{17}H_{14}O_4N_2S$	Fine rosy	140°	170°	S. 9·51	9·35
Acetone dicarboxy-*o*-toluidide-S	$C_{19}H_{18}O_4N_2S$	Pink	155-56°	174°	S, 8 45	8 64
Acetone dicarboxy-*p*-toluidide-S	$C_{19}H_{18}O_4N_2S$	Pink	185°	208-10°	S, 8·29	8·64
Acetone dicarboxy-α-naphthylamide-S	$C_{25}H_{18}O_4N_2S$	Greenish brown	137°	155°	S, 7·59	7·24
Acetone dicarboxy-β-naphthylamide-S	$C_{25}H_{18}O_4N_2S$	Crimson	185°	207°	S, 6 99	7·24

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CHEMISTRY DEPARTMENT,
THE COLLEGE, BARODA.

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XXVI. A study of the Interaction between Thionyl Chloride and Substances Containing the Reactive Methylene(-CH_2-) Group. Part IV.

By K. G. Naik and V. B. Thosar.

A close study of the reactions of thionyl chloride with organic compounds clearly shows that the course of reaction followed by thionyl chloride is entirely guided by the conditions of experiment in many cases. The reaction of thionyl chloride with phenols, phenetoles and alcohols might be cited as examples of this type. Generally in presence of anhydrous aluminium chloride, these compounds give rise to sulphides. But by slightly changing the conditions of the experiment, the same reaction can be made to follow a different course, as a result of which sulphoxides are obtained (Loth and Michaelis, *Ber.*, 1894, **27**, 2540; Smiles and Rossignol, *J. Chem. Soc.*, 1908, **93**, 745). Hence it was thought interesting to examine the course of the reaction followed by thionyl chloride when it reacts with substances containing a reactive methylene (-CH_2-) group in *cold ethereal solution*, although a similar reaction in *boiling benzene solution* had already resulted in the formation of sulphoxides (Naik, Desai and Parekh, *J. Indian Chem. Soc.*, 1930, **7**, 137; Naik and Thosar, *ibid.*, 1932, **9**, 127); and as will be seen from the experiments recorded in this paper this expectation is completely fulfilled.

Thionyl chloride was made to react with the following amides in presence of *cold* anhydrous ether.

(1) Acetoacetanilide, (2) acetoacet-*o*-toluidide, (3) acetoacet-*m*-toluidide, (4) acetoacet *p*-toluidide, (5) acetoacet-β-naphthylamide, (6) acetoacet-1 : 3 : 4-xylidide, (7) malondi-*n*-propylamide, (8) malondi-*iso*butylamide, (9) malondiamylamide, (10) malondiheptylamide, (11) ethylmalon-*o*-tolylamate. (12) ethylmalon-*p*-tolylamate, (13) ethylmalon-β-naphthylamate, (14) ethylmalon-1 : 3 : 4 :-xylilamate, (15) ethylmalon-1 : 4 : 5 xylilamate.

The amides slowly went into solution, from which sulphides began to separate out, the reaction being complete after

several days, the time required depending upon the nature of the amide used. Amides (1) to (10) gave sulphides of the general constitution,

$$\begin{matrix}R'\cdot CO\\ RNH\cdot CO\end{matrix}>CH{-}S{-}HC<\begin{matrix}CO\cdot R'\\ CO\cdot NHR\end{matrix}$$

(where R=phenyl, tolyl, naphthyl, xylil or propyl groups and R' is either a CH_3 or -NHR group); but in the case of amides (9) and (10) the reaction products were liquids which did not solidify even when placed in a freezing mixture. They will be worked up later. On the other hand the amates (11) to (15) gave sulphides of the formula

$$S:C<\begin{matrix}CO\cdot NHR\\ CO\cdot OC_2H_5\end{matrix}$$

The above constitution of these sulphides follows from the following considerations :

(*i*) That the two hydrogen atoms are not supplied by the phenyl group, since (*a*) acetoacetic ester, which does not contain such a phenyl group reacts with thionyl chloride in a similar manner (Michaelis and Philips, *Ber.*, 1890, **23**, 559); (*b*) malondi-*n*-propylamide containing no phenyl nucleus also reacts with thionyl chloride to give a similar compound.

(*ii*) That the hydrogen atoms eliminated are not those, which are originally attached to the nitrogen atom of -NHR group, for (*a*) ethyl acetoacetate which does not contain such a hydrogen atom reacts similarly with thionyl chloride; (*b*) in case of malondi-*n*-propylamide which contains two such amido hydrogen atoms only one is replaced. On the supposition that the hydrogen atom of the -NHR group is reactive both these hydrogen atoms must react.

Finally in order to establish that these compounds are not sulphoxides of the formula

$$\begin{matrix}R'\cdot CO\\ RNH\cdot CO\end{matrix}>CH{-}\underset{\|}{S}{-}HC<\begin{matrix}CO\cdot R'\\ CO\cdot NHR\end{matrix}$$

advantage was taken of the fact that Michaelis and Philips had actually obtained a sulphide of acetoacetic ester by the action of thionyl chloride upon it (*loc. cit.*). As the conditions used by these authors were slightly different from those used here, thionyl chloride was made to react with acetoacetic ester under exactly the same conditions as were used here and it was found that the product obtained was identical with that obtained by the above authors. This sulphide of acetoacetic ester has been prepared by a host of workers from various sources so as to leave no doubt as to its constitution (Buchka, *Ber.*, 1885, **18**, 2092; Delisle, *ibid.*, 1889. **22**, 306; Schonbrodt, *Annalen*, 1889, **253**, 198; Sprague, *J. Chem. Soc.*, 1891, **59**, 329).

The reaction of thionyl chloride with amates (11) to (15) is also in favour of the sulphide constitution for the following reasons :

(*i*) These amates, when they were made to react with thionyl chloride in *boiling benzene*, where there is a greater possibility of the formation of sulphoxides, gave rise to liquid products (Naik, Desai and Parekh, *loc, cit.*).

(*ii*) The reaction products obtained here are white crystalline substances, whereas the sulphoxides of the linking : C : S : O obtained till now are always coloured substances.

Michaelis and Philips (*loc. cit.*) hold that in such reactions, thionyl chloride behaves as if it were a mixture of sulphur dichloride and sulphuryl chloride, 2 $SOCl_2 \rightarrow SCl_2, SO_2Cl_2$, sulphur dichloride reacting with acetoacetic ester with the formation of the above sulphide. This view is further confirmed by the reaction of thionyl chloride with aromatic tertiary amines yielding two different products as represented by the equations :

$$3PhN(CH_3)+2SOCl_2=S[C_6H_4N(CH_3)_2]_2+SO_2<\begin{matrix}C_6H_4N(CH_3)_2\\Cl\end{matrix}+3HCl$$

the second product being obtained by the action of sulphuryl chloride (SO_2Cl_2) on the amine (Michaelis and Godchaux, *Ber.*, 1890, **23**, 553). The reaction of thionyl chloride with phenol

also gives a sulphide together with other substances containing both sulphur and chlorine (Tassinari, *Gazzetta*, 1890, **20** 362).

The same explanation can very well be given in the reaction studied here.

$$2\left[\begin{matrix} R\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>CH_2\right] + 2SOCl_2 \rightarrow 2\left[\begin{matrix} R'\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>CH_2\right] + SCl_2,$$

$$SO_2Cl_2 \rightarrow \begin{matrix} R'\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>CH-S-HC\!\!<\begin{matrix} CO\cdot R' \\ CO\cdot NHR \end{matrix} + SO_2Cl_2 + 2HCl$$

The course of the reaction followed by SO_2Cl_2 cannot be definitely ascertained here, as the mother liquor on evaporation gives only a semi solid mass, which it is proposed to work up later. In all probability the course followed by the reaction is different from that followed under ordinary conditions where chloro compounds are obtained (Naik and Shah, *J. Indian Chem. Soc.*, 1927, **4**, 11). It is just possible that the catalytic action of thionyl chloride might again play its important part here and give rise to compounds of the type obtained in the case of tertiary amines and phenols.

The reaction in the case of amates (11) to (15) can be represented as

$$\begin{matrix} C_2H_5O\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>CH_2 + 2SOCl_2 \rightarrow \begin{matrix} C_2H_5O\cdot CO \\ RNH\cdot CO \end{matrix}\!\!>C:S + 2HCl + SO_2Cl_2.$$

Such a course of reaction is not an abnormal one. Many instances can be cited where under similar conditions both the hydrogen atoms of the methylene group of the amates react, whereas usually only one hydrogen atom of the methylene group in the case of the aliphatic amides of malonic acid is found to react (Naik, *J. Chem. Soc*, 1921, **119**, 379; West, *ibid.*, 1922, **121**, 2196; Naik and Shah, *J. Indian Chem. Soc.*, 1930, **7** 111; Naik and Shah, *ibid.*, 1927, **4** 11; Norris and Thorpe, *J. Chem. Soc.*, 1921, **119**. 1223). The course of reaction where only one hydrogen atom takes part, is explained by supposing that the second hydrogen atom becomes sluggish after the first is replaced by a substituent.

From the consideration of the time taken to complete the reaction (*vide* experimental) in a series such as,

$$H_2C\begin{array}{l}\diagup COCH_3 \\ \diagdown CO\,NHR\end{array} \qquad H_2C\begin{array}{l}\diagup CO{\cdot}OC_2H_5 \\ \diagdown CO{\cdot}NHR\end{array} \qquad H_2C\begin{array}{l}\diagup CO{\cdot}NHR \\ \diagdown CO{\cdot}NHR\end{array}$$

(I) (II) (III)

the time required for the completion of the reaction in the case of the type (III) is longer than that required in the case of type (II), which in its own turn was found to be less reactive than type (I). This is quite in accord with the hypothesis put forward by Naik (*J. Chem. Soc.*, 1921, **119**, 1166), and supported by the experimental work carried on in these laboratories since then. That the compounds of type (II) are less reactive than those of type (I) follows from the fact that the total negativity of the adjoining carbonyl groups in type (II) is made smaller than that in type (I), by the replacement of a carbethoxy group in place of acetyl group, the other (-CONHR) group being common to all the three types. This total negativity is still further reduced in compounds of the type (III) where both the carbonyl groups are partially neutralised by the -NHR group and hence in this case the reactivity of the hydrogen atoms of the methylene group is the least and the time required for the completion of the reaction longest.

On examining the properties of these compounds it was found that the thio grouping (-S-) in these compounds is not so stable as the thio grouping in the componnds obtained by Naik by the action of sulphur monochloride on substances containing the reactive methylene group (*J. Chem. Soc.*, 1921, **119**, 1166 1231). Thus, while the dithio grouping is quite unaffected by fuming nitric acid and silver nitrate, the thio grouping in these compounds is destroyed, giving rise to free sulphuric acid in the first case, and silver sulphide in the other. The sulphides derived from amates are still more unstable and are gradually decomposed on keeping for a long time.

EXPERIMENTAL.

Thiobisacetoacetanilide—Thionyl chloride (2·5 g.) was added to pure dry acetoacetanilide (3·5 g.) suspended in dry ether (30 c. c) in a conical flask tightly corked with a calcium chloride tube to avoid moisture and left at room temperature(28-30) The amide slowly went in solution (3 hours) and the ethereal solution attained a rich red colour. On the next day white hexagonal plates began to separate out. After 3 days, when the reaction was complete the separated solid was filtered at the pump and washed with dry ether to free it from the excess of thionyl chloride. After crystallising it from a mixture of benzene and light petroleum (b p. 50-60°) the substance was obtained in the form of white, hard prismatic needles, m. p. 132°. But this substance was found to contain traces of hydrochloric acid from which, it could not be freed even on repeated crystallisations or keeping it in an alkali desiccator for a long time. The melting point also remained unchanged. Hence the substance was dissolved in benzene and boiled with a small amount of animal charcoal (0·2 g.) under reflux for nearly 6 hours. The clear filtrate from animal charcoal was allowed to cool after adding an equal amount of dry light petroleum. The resulting product was now free from hydrochloric acid and was obtained in the form of white silky needles, m. p. 147. It is interesting to note here that the impure compound had the same melting point (132°) in whatever conditions it was taken out of the reaction mixture. The analysis of the impure substances also amounted to nearly 1 mol. of hydrochloric acid in combination with 1 mol. of the sulphide.

The substance is readily soluble in benzene, sparingly so in chloroform, carbon tetrachloride, carbon disulphide and insoluble in petroleum ether and ether. (Found : N, 7·25; S, 7·90. $C_{20}H_{20}O_4N_2S$ requires N, 7·29; S, 8·33 per cent.)

All other sulphides were similarly prepared by treating the respective amides with thionyl chloride under the above conditions. A slight excess of thionyl chloride than required by

equation was always necessary to compensate for the loss caused by gradual decomposition. All the sulphides except those obtained from amates had to be purified by boiling with animal charcoal for 6 hours. The results of these experiments are tabulated in Table I.

Hydrolysis of thiobisacetoacet-β-naphthylamide-The compound (3 g.) was added to the solution of caustic potash (7 g.) in water (8 c. c.) and refluxed for 2 hours. The mixture was cooled and filtered. It was washed with cold water till it was free from alkali. The solid was crystallised from hot water, when characteristic rosy leaflets separated out, m. p. 111°. The substance was identified as β-naphthylamine and confirmed by mixed melting point. The filtrate was evaporated to dryness on a water bath and the solid obtained was treated with hydrochloric acid when H_2S was found to evolve.

TABLE I.

[T=Thiobisaceto ; D=Thiobismalon ; E=Ethylmalon]

Name	Formula.	Appearance.	M.p.	Duration of reaction (days)	Analysis Found.	Analysis Calc.
T-acetanilide	$C_{20}H_{20}O_4N_2S$	Silky needles	147°	3	S,7·90	8·3p.c.
T-*o*-toluidide					N,7·3	7·29
	$C_{22}H_{24}O_4N_2S$	Light flakes	160°	3	S,7·6	7·76
T-*m*-toluidide					N,6·6	6·79
	$C_{22}H_{24}O_4N_2S$	Prismatic needles	104°	3	S,7·52	7·76
T-*p*-toluidide	$C_{22}H_{21}O_4N_2S$	Silky needles	174°	3	S,7·68	7·76
T-β-naphthylamide	$C_{28}H_{24}O_4N_2S$	Light tufts	185°	4	S,7·26	6·61
T-(1 : 3 : 4)-xylilamide	$C_{24}H_{28}O_4N_6S$	Shining light tufts	139°	3	S,7·32	7·21
D-di-*n*-propylamide	$C_{18}H_{34}O_4N_4S$	Short needles	123°	10	S,8·05	7·95
D-di-*iso*butylamide	$C_{22}H_{42}O_4N_4S$	Light tufts	155°	12	S,6·69	6·98
E-*o*-tolylamate sulphide	$C_{12}H_{13}O_3NS$	Small prisms	196°	6	S,12·4	12·7
E-*p*-tolylamate sulphide	$C_{12}H_{13}O_3NS$	Hard needles	203°	6	S,12·45	12·7
E-β-naphthylamate sulphide	$C_{15}H_{13}O_3NS$	Silky needles	208°	6	S,11·01	11·14
E-1 : 3 : 4-xylilamate sulphide	$C_{13}H_{15}O_3NS$	Light tufts	175°	6	S,11·79	12·08
E-1 : 4 : 5-xylilamate sulphide	$C_{13}H_{45}O_3NS$	Short crystals	187°	6	S,11·88	12·08

The authors take this opportunity to express their gratitude to the Government of His Highness the Maharaja Geakwar of Baroda, for a grant which defrayed the expenses incurred in this work.

CHEMISTRY DEPARTMENT,
BARODA COLLEGE,-BARODA.

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XXVII Mercuration of Compounds Containing a Reactive Methylene ($-CH_2$) Group by means of Mercuric Chloride. Part II.

BY : K. G. NAIK AND R. P. PATEL.

It is well known that when an aqueous solution of mercuric chloride is boiled with sodium bicarbonate, mercuric oxychlorides are precipitated (Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1923, Vol. IV, p. 833; Millon, *Ann. chim. phys.*, 1846, *iii*, **18**, 372). These oxychlorides differ in their composition according to the experimental conditions and are usually expressed as double compounds of mercuric chloride and mercuric oxide. But it is possible to conceive that when to a boiling aqueous alcoholic solution of mercuric chloride and a reacting organic compound, a solution of sodium bicarbonate is added, the above double compounds of mercury, no sooner are they formed in an incipient condition than, would react with the organic compound present. With such a possibility, the organic compounds containing a reactive methylene group would, under the above conditions, give products containing the grouping $>C : Hg$. Such has actually been found to be the case.

The course of reaction may be expressed as ;

$$HgCl_2 + NaHCO_3 \longrightarrow m{\cdot}HgCl_2{\cdot}n{\cdot}HgO$$

$$n\ {}^{R}_{R}\!\!>C\boxed{H_2 + n{\cdot}O}Hg{\cdot}m\ HgCl_2 \longrightarrow n\ {}^{R}_{R}\!\!>C : Hg$$

The following substituted amides of malonic acid and acetoacetic acid when mercurated under the above conditions, gave products of the general formula :

$$Hg : C\!\!<\!\!{}^{CO-}_{CO-}$$

(1) Malonmonophenylamide, (2) malonmono-*o*-toluidide, malonmono-*p*-toluidide, (4) malonmono-*m*-toluidide, (5) malonmono-α-naphthylamide, (6) malonmono β-naphthylamide, (7)

malonmono-1 : 3 : 4-xylidide, (8) malonamide, (9) ethyl malonate, (10) ethyl aceto-acetate, (11) acetoacetanilide, (12) acetoacet-*o*-toluidide, and (13) acetoacet-*p*-toluidide.

That the compounds obtained do not contain admixed mercuric oxychlorides, is shown by the fact that they come out of the mixture as white precipitates which when separated and analysed were found to contain no chlorine; and at no time during the reaction was any change of colour observed. Furthermore, the mercury derivatives were insoluble in the ordinary solvents, whereas the original amides are quite soluble.

The resultant products decompose on treatment with dilute 0·25*N*-hydrochloric acid giving the original amide and mercuric chloride. With hydrogen sulphide they react quantitatively giving black mercuric sulphide. Potassium iodide decomposes the compounds forming the original amide and at the same time liberating two equivalents of alkali for each molecule of the product. Phenylhydrazine and hydrazine hydrate decompose the above compounds with the separation of metallic mercury. The above reactions clearly indicate the existence of a weak C—Hg linkage, which is usually found in compounds, containing mercury attached to a carbon atom in α-position to a carbonyl group.

From considerations such as (*a*) the formation of a mercury derivative from ethyl acetoacetate and ethyl malonate, (*b*) the nonrupture of the C—Hg linkage under conditions which invole the rupture of N—Hg linkage (Ley and Kissel, *Ber.*, 1899, **32**, 1357), (*c*) the behaviour of the resultant compounds in a way similar to those having mercury attached to a carbon atom in α-position to a carbonyl group (Billman, *Ber.*, 1902, **35**, 2582; Schoeller and Schrauth, *Ber*, 1908 **41**, 2091; Petterson *J. pr. Chem.*, 1912, *ii*, **86**, 498; Schrauth and Bauerschmidt, *Ber.*, 914, **47** 2740); (*d*) the quantitative decomposition by potassium iodide, and (*e*) the formation of dibromomalonamide, with bromine as advanced in a previous communication (Naik and Patel, *J. Indian Chem. Soc*, 1932, **9**, 185), the above constitution has been assigned to the compounds described herein.

EXPERIMENTAL.

Mercurimalonmonophenylamide, (I)—Malonmonophenylamide (1 g.) and mercuric chloride (1·15 g.) were dissolved in alcohol and the solution heated to boiling in a flask. To the hot solution was added a solution of sodium bicarbonate (1 g.). The solution became turbid as the compound began to separate and there was effervescence due to the escape of carbon dioxide. The flask was then heated for ½ hour to complete the reaction. The precipitate was then filtered hot at the pump, washed thoroughly with the alcohol and subsequently with water. The product is insoluble in most of the ordinary organic solvents. It melts with decomposition at 275-78°. (Found : N, 7·25; Hg, 53·29. $C_9H_8O_2N_2Hg$ requires N, 7·44; Hg. 53·19 per cent.).

Action of dilute hydrochloric acid on (I).—The compound (I) on treatment with hot 0·25*N*-HCl went into solution which when concentrated and cooled deposited crystals of malonmonophenylamide, m. p. 164°.

Action of hydrogen sulphide on (I).—The compound (I) (0·6039 g.) was suspened in 30 p. c. alcohol and a slow current of hydrogen sulphide gas was passed into the solution till the precipitation of mercury as mercuric sulphide was complete. The precipitates were then filtered through a Gooch crucible and washed repeatedly with alcohol and water till free from hydrogen sulphide and the amide formed by the decomposition of the compound. It was then washed with carbon disulphide (20 c. c.) and pyridine (20 c. c.) to remove the sulphur which might have been precipitated together with mercuric sulphide. It was finally washed with alcohol and ether to remove the adhering carbon disulphide and pyridine, dried at 105-10° and weighed (0·3762 g.). (Found : Hg, 53·69. $C_9H_8O_2N_2Hg$ requires Hg, 53·19 per cent.).

This indicates that the decomposition of the substance with hydrogen sulphide was quantitative.

Action of phenylhydrazine and hydrazine hydrate.—The compound (I) was decomposed when it was treated either with

phenylhydrazine or with hydrazine hydrate with the separation of grey metallic mercury which settled down.

Action of bromine on mercurimalonamide.—The mercury derivative suspended in water was treated with an aqueous solution of bromine till no more bromine was absorbed. The flask was then heated to boiling and the solution concentrated. On cooling crystalline precipitates of the bromo-derivative and mercuric bromide were obtained. The precipitates were then filtered and washed with alcohol till free from mercuric bromide. The residue when dried melted at 203·04°. It was identical with the dibromomalonamide obtained by the direct bromination of malonamide (Freund, *Ber* 1884, **17**, 782).

Mercurimalonmono-o-toluidide, (II).—This was prepared in exactly the same way as the corresponding malonmonophenylamide derivative (I). The product is insoluble in all the ordinary organic solvents and melts with decomposition at 257-59°. (Found : Hg, 51·6. $C_{10}H_{10}O_2N_2Hg$ requires Hg 51·3 per cent.).

Action of potassium iodide on (II).—The compound (II) (0·28 g.) suspended in water was treated with an aqueous solution of potassium iodide (1 g.). Potassium hydroxide was gradually liberated. After a day, the liberated potassium hydroxide was titrated against 0·059*N*-HCl (23·3 c. c.). It was found that no more potassium hydroxide was liberated, even on further heating the mixture, showing that the reaction was complete in the cold.

The liberation of 1·915 equivalents of alkali indicates that the rupture of C–Hg linkage is almost quantitative in the cold.

Compounds similar to the above have been prepared by the interaction of the compounds (3) to (13) with mercuric chloride in presence of sodium bicarbonate under identical conditions. These have been tabulated in the annexed table.

Reaction products of mercuric chloride with substances containing the reactive methylene group.

(M = Mercurimalonmono—)

Name.	Formula.	M. p. (with decomp).	Analysis. Found.	Analysis. Calc.
M-phenylamide	$C_9H_8O_2N_2Hg$	275-78°	Hg, 53·29 N. 7·25	53·19 p. c. 7·44
M-*o*-toluidide	$C_{10}H_{10}O_2N_2Hg$	257-59°	Hg, 51·6	51·3
M-*p*-toluidide	$C_{10}H_{10}O_2N_2Hg$	278-79°	Hg, 50·8	51·3
M-*m*-toluidide	$C_{10}H_{10}O_2N_2Hg$	25[illegible]°	Hg, 50·9	51·3
M-∝-naphthylamide	$C_{13}H_{10}O_2N_2Hg$	269°	Hg, 47·4	46·94
M-β-naphthylamide	$C_{13}H_{10}O_2N_2Hg$	270°	Hg, 47·43	46·94
M-(1 : 3 : 4)-xylidide	$C_{11}H_{12}O_2N_2Hg$	27[illegible]°	Hg, 49·2	4[illegible]·5
Mercurimalonamide	$C_3H_4O_2N_2Hg$	28[illegible]°	Hg, 66·62	66·66
Mercuriethylmalonate	$C_7H_{10}O_4Hg$	Does not decompose till 300°	Hg, 56·01	55·85
Mercuriethylacetoacetate	$C_6H_8O_3Hg$	Turns brownish black above 270°	Hg, 60·5	60·93
Mercuriacetoacetanilide	$C_{10}H_9O_2NHg$	205°	Hg, 53·36	53·33
Mercuriacetoacet-*o*-toluidide ...	$C_{11}H_{11}O_2NHg$	230°	Hg, 51·75	51·4
Mercuriacetoacet-*p*-toluidide ...	$C_{11}H_{11}O_2NHg$	243-[illegible]7°	Hg, 51·3 N, 3·95	51·4 3·59

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CHEMISTRY DEPARTMENT,
THE COLLEGE, BARODA.

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XVIII—Properties of Conjugated Compounds. Part XII. The Addition of Esters to Butadiene Esters and Ketones: the Effect of Constitution on the $\alpha\beta$, $\alpha\delta$-Ratio.

By Ernest Harold Farmer and Thakorbhai Naranji Mehta.

The study of ester addition is a useful means of determining the extent to which the additive mode of butadienoid compounds is dependent on constitutive factors. The Michael reaction affords the advantages of fairly constant conditions of operation over a wide range of examples, and a high degree of stability in the end products; consequently it seemed possible to follow experimentally the variation in additive mode with (1) change in the alkyl (or other) substituent in the butadiene chain, (2) modification of the activating group attached to the α-carbon atom of the butadiene chain, and (3) graduated modification of the addendum. The utility of the process as a source of accurate comparative data has, in practice, been greatly diminished by the difficulty of separating, estimating, or even recognising the presence of the isomeric compounds which should result from the simultaneous occurrence of different additive modes; indeed, owing to this difficulty, the concurrent production of both $\alpha\beta$- and $\alpha\delta$-ester-addition products has only recently been demonstrated (Farmer and Mehta, J., 1930, 1610). The compounds which should arise by interaction of the simpler butadiene esters and ketones with common ester-or keto-addenda are for the most part unknown and difficult of synthesis; consequently, separative methods offer at present the only practicable means of computing the ratio of isomeric addition products. The present paper describes an attempt to overcome the experimental difficulties (compare Farmer and Mehta, *loc. cit.*) sufficiently to obtain reasonably accurate estimates of the $\alpha\beta$, $\alpha\delta$-ratio holding for a number of alkylated butadiene esters and ketones.

Of the two methods previously employed in computing the ratio, *viz.*, (*a*) the quantitative estimation of the proportion

in which acids of the glutaric and pimelic series can be obtained from the catalytically reduced addition products, and (*b*) the separation of suitable derivatives of the ozonolytic degradation products of the respective additive compounds, only the first could be successfully applied to the product from methyl sorbate and methyl malonate. The same method, however, proved unsuitable when applied to the product from ethyl γ-methylsorbate and ethyl cyanoacetate, the presence of the γ-methyl group in the addition product appearing effectively to inhibit the catalytic reduction of $\beta\gamma$- and $\gamma\delta$-double-bonded addition products under conveniently accessible conditions of temperature and pressure. A similar resistance to catalytic reduction appears from recent work to characterise the presence of a β-methyl group in the addition product; therefore, as no type of simple derivative *generally* suited to the separation of isomeric addition products has been discovered, it has been necessary, in order to deal with instances in which the reductive method fails, to improve the ozonolytic method.

This method of estimation, being degradative, requires the employment of much larger quantities of starting material than the reductive method; moreover, the $\alpha\beta$-addition products of the series yield ultimately, by degradation, acids of the tricarballylic group which are extremely liable to escape isolation. By improving the method of extracting these acids, whilst employing larger quantities of addition product than formerly, it has been possible to increase the total yield of separated degradation products, but this yield does not exceed 63%. There is a possibility, therefore, that the figures obtained by the two methods are not comparable, *i. e.*, that the losses incurred by employing the ozonolytic method apply unequally to the respective degradation products of $\alpha\beta$- and $\alpha\delta$-forms. This does not appear, however, to be generally or seriously the case, since the values of the $\alpha\beta,\alpha\delta$-ratio determined by the two methods for the additions of methyl malonate to methyl

sorbate and to crotylideneacetone are almost identical in each case. The table shows the effect on the percentage of the $\alpha\beta$-addition product of (*a*) methyl substitution at the β- and γ-atoms of the butadiene chain in sorbic ester* and (*b*) change of the activating group from carbomethoxyl to acetyl.

Reaction.	Method of treatment.	Yield of isolated material, %	Proportion of $\alpha\beta$-form.
1. Methyl sorbate + methyl malonate	(i) Ozonolysis	60	9
	(ii) Hydrogenation	90	7—10
2. Ethyl β-methylsorbate + ethyl malonate	Ozonolysis	62	<7*
3. Ethyl γ-methylsorbate + ethyl cyanoacetate	(i) Hydrolysis and ozonolysis	64	74·5
	(ii) Ozonolysis	76	70
4. Crotylideneacetone + methyl malonate	(i) Ozonolysis	67	27
	(ii) Hydrogenation.	90	29

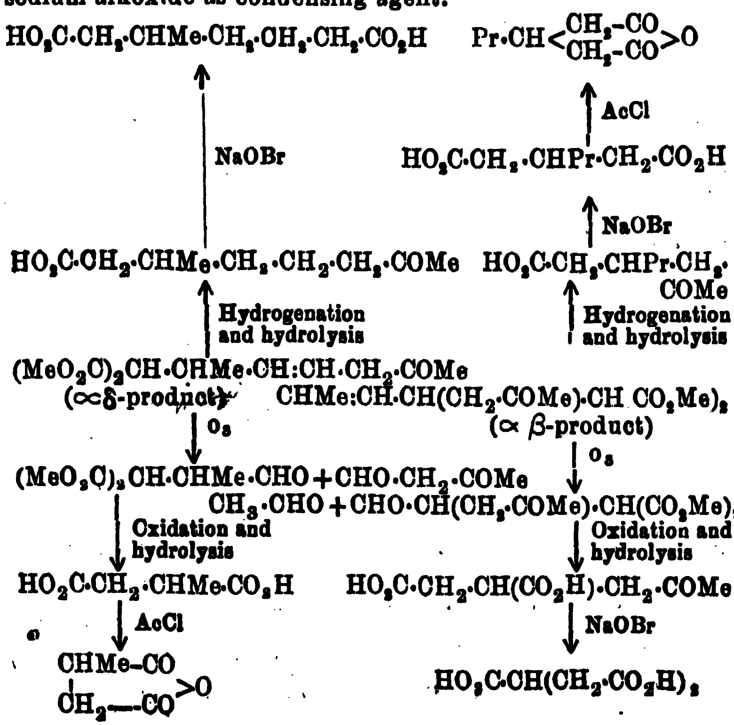
*Farmer and Mehta, *loc. cit.*

The numerical values appear to have a well-defined constitutional significance. At present, however, it is difficult to correlate the low ratios found for the δ-methyl and $\beta\delta$-dimethylbutadiene esters, and the high ratios for the analogous $\gamma\delta$-dimethyl compound. with such detailed views on the relative activating and modifying powers of groups situated at the different carbon atoms of the three-carbon system as have been expressed in connexion with the principle of mobile ion tautomerism (see Ingold, *Ann. Reports*, 1928 **25**, 127). Further comment on this question is, therefore, postponed pending investigation of the way in which the

* Methyl substitution at both β-and δ-carbon atoms of sorbic ester totally inhibits addition, so that the joint effect of β- and δ-alkyl substituents has been unascertainable It seems probable from recorded observations (Kohler and Butler, *J. Amer. Chem. Soc.*, 1926, **48**, 1036; Farmer and Healey, J., 1927, 1060) that the amount of the $\alpha\beta$-isomeride from the parent butadiene ester (β-vinylacrylic ester) amounts at most to one or two units%.

ratio varies with changes in the activating group attached to butadiene system. It is clear that the nature of the activating group is not without some effect in determining the proportion between isomeric forms of the addition product; indeed, the alteration in the ratio consequent on change from CO_2Et to COMe is so great that comparisons between different types of butadienoid compounds (esters, ketones, nitriles, etc.) would seem to be invalidated.

It should be noted that the addendum in the instance of ethyl γ-methylsorbate was ethyl cyanoacetate and not ethyl malonate. Presumably the $\alpha\beta,\alpha\delta$-ratio of an alkylated sorbic ester is independent of the constitution of the particular ester- or keto-addendum employed in its determination, but the point is being tested experimentally. It should also be noted that the ester additions described in this series of papers have all been carried out under "catalytic" conditions of operation, *i. e.*, with only a small proportion of sodium alkoxide as condensing agent.



Since the more important details connected with the reduction and degradation of the addition products from methyl sorbate and ethyl γ-methylsorbate have already been described, it is only necessary to refer to the method of dealing with the products from crotylideneacetone and ethyl β-methylsorbate. The $\alpha\beta,\alpha\delta$-ratio for the former was determined (*a*) by weighing the amount of β-propylglutaric acid (isolated from its mixture with β-methylpimelic acid) derivable from a weighed amount of the catalytically reduced addition product, and (*b*) by estimating the proportions of tricarballylic acid and methylsuccinic anhydride obtainable by the decomposition of a weighed amount of the addition product. The stages passed through in attaining the end products are indicated in the scheme above.

The addition products from ethyl β-methylsorbate should yield by degradation β-methyltricarballylic acid and methylsuccinic acid. The latter was readily isolated, but the presence of β-methyltricarballylic acid remained undetected. This acid is doubtless produced in very small amount, since its complementary degradation product, acetaldehyde, is detectable, but in view of the fact that it should be more readily extracted from the oxidation residues than tricarballylic acid and that the latter has been isolated in a proportion corresponding to 7% of an $\alpha\beta$-addition product, there is every reason to believe that the proportion of $\alpha\beta$-addition product in this instance does not exceed, and is probably considerably less than, 7%.

EXPERIMENTAL.

Addition of Methyl Malonate to Methyl Sorbate.—The mixture of addition products (compare Farmer and Mehta, *loc. cit.*) (32 g.), dissolved in chloroform, was ozonised at 0° until no more ozone was absorbed. Removal of the solvent from the product yielded a viscous ozonide which was gently heated with water (40 c.c.) to about 70°, the vapours generat-

ed in the reaction vessel being swept by a slow stream of carbon dioxide into a saturated solution of 5:5-dimethyl*cyclo*hexane-1:3-dione. After a few minutes a precipitate began to form in the latter solution; this, after being washed with water, melted at 139° and was found to be the acetaldehyde derivative of dimethyl*cyclo*hexanedione (mixed m. p. 139°).

The aqueous reaction product, which gave an intense colour with ferric chloride, indicating the presence of formylacetic ester or its polymeride, γ-formylglutaconic ester, was ultimately heated for 2 hours on a sand-bath in order to decompose any residual ozonide. The aldehydic esters contained in the product were oxidised with 30% hydrogen peroxide (40 c. c.), the mixture being kept at room temperature with occasional shaking until the product no longer gave a coloration with Schiff's reagent (2 days). The acid reaction product, when made alkaline with sodium carbonate and shaken with ether, yielded no neutral (unoxidised) material. The dissolved acid esters were hydrolysed by heating with the calculated quantity of caustic soda solution and then decarboxylated by refluxing for 12 hours with approximately 20% hydrochloric acid. The resulting liquor was extracted 10 times with ether, evaporated to dryness, and the residue exhaustively extracted with ether. The final residue was heated for some time at 180° to convert any polybasic acids into their anhydrides, and then thoroughly extracted with ether. The first and second of these extracts yielded crude methylsuccinic acid; the third contained no dissolved material. Since in none of the degradations of the sorbic ester addition product previously carried out had separation of even a small quantity of tricarballylic acid from the crude methylsuccinic acid been achieved by fractional crystallisation, the whole of the acid material was heated with acetyl chloride for 3 hours. Removal of excess acetyl chloride by distillation, and of acetic acid by keeping the residue over caustic soda in a vacuum desiccator,

yielded an anhydride which was separated by distillation into two portions, (i) b. p. 112—115°/7 mm. and (ii) b. p. 220—225°/7 mm. The first fraction yielded methylsuccinic acid on boiling with water (m. p. and mixed m. p. 111°; equiv., 66), and the second, which solidified in the receiver (m. p. 131° after recrystallisation from acetic acid-chloroform), gave tricarballylic acid (m. p. and mixed m. p. 160°; equiv., 58·3) on boiling with water. Yields: methylsuccinic acid, 9 g.; tricarballylic acid, 1·2 g.

Addition of Methyl Malonate to Crotylideneacetone.—The *additive process.* The addition product was obtained by warming gently on a steam-bath for 7 hours the mixture obtained by adding successively methyl malonate (50 g.), sufficient dry ether to produce turbidity (about 10 c. c.), and crotylideneacetone (24 g.) to a solution of sodium (0·6 g.) in the minimal quantity of methyl alcohol (about 6 c. c.). The product was cooled, poured into water, and extracted with ether. The dried ethereal extract yielded (i) unchanged reactants which distilled below 100°/18 mm., (ii) the addition product, a colourless oil, b. p. 170—175°/18 mm., and (iii) high-boiling material which constituted only a small proportion of the whole except when the additive process was unduly prolonged. The addition product, obtained in 66% yield, was shown as described below to be a mixture of the isomeric substances *methyl β-acetonyl-Δ^{γ}-pentene-αα-dicarboxylate* and *methyl β-methyl-ε-acetyl-Δ^{γ}-pentene-αα-dicarboxylate* (Found: C, 59·3; H, 7·3. $C_{12}H_{18}O_5$ requires C, 59·5; H, 7·4%).

Hydrogenation of addition products. The addition product (24 g.) was dissolved in aqueous methyl alcohol and shaken with hydrogen in the presence of colloidal palladium and gum arabic: it was necessary to renew the catalyst several times in order to ensure the absorption of a molecular proportion of hydrogen. The reduction product, worked up in the usual way, was a colourless oil, b. p. 158—163°/12 mm.; yield quantitative.

Acids derived from the hydrogenation product.—The reduction product was boiled for 12 hours with 4 times its volume of 20% hydrochloric acid. The resulting solution was first extracted 6 times with ether and then evaporated to dryness, the residue being taken up in ether. From the ethereal liquors an almost quantitative yield of syrupy ketonic acid was obtained.

Since the ketonic hydrolysis product could not be directly resolved into its component acids, it was oxidised by dissolving it (17 g.) in cold dilute potash solution and gradually adding it with shaking to a hypobromite solution (bromine, 20 c. c.; potassium hydroxide, 45 g.; water 250 c. c.). The resulting solution, from which bromoform soon separated, was kept over-night, treated with sodium sulphite, evaporated to dryness, acidified with hydrochloric acid, and extracted thoroughly with ether. From the ethereal extract a syrupy mixture of isomeric acids was obtained in about 90% yield. Separation of the acids was achieved by distillation, the portion distilling at 163—165°/10 mm. consisting of β-propylglutaric anhydride admixed with a little β-methylpimelic acid, and that distilling at 195—200/10 mm. consisting of β-methylpimelic acid, m. p. 47° (mixed m. p. 47°); the calcium salt of the latter readily yielded, on heating, 3-methyl*cyclo*hexan-1-one, b. p. 160—165° (semicarbazone, m. p. 191°). The β-propylglutaric acid was purified by converting it into its anhydride by means of acetyl chloride and boiling the pure anhydride (b. p. 181—183°/23 mm.) with water; the regenerated acid, after recrystallisation from dilute hydrochloric acid, melted at 52° (mixed m. p. 52°), and its anilic acid at 128° (mixed m. p. 128°). The total yield of β-propylglutaric acid from 15 g. of the mixed acids was 4·4 g., corresponding to a proportion of $\alpha\beta$-addition products of 29·3%.

Ozonolysis of the addition product. A further portion of the addition product (37 g.) was ozonised as described above. Considerable acetaldehyde was generated (dimethone, m. p.

and mixed m. p. 139°;, and the aqueous recetion product gave, as would be expected if an $\alpha\delta$-addition product were present originally, a deep colour with ferric chloride. The aldehydic esters were oxidised with hydrogen peroxide as described above, and then heated with 15% hydrochloric acid for 24 hours. The aqueous acid liquor was thoroughly extracted with ether, and then evaporated to dryness, and the residue taken up in ether. The dried ethereal liquors yielded an acid syrup which was heated with acetyl chloride for 3 hours, and ~~then,~~ after removal of the reagent and acetic acid, distilled, giving methylsuccinic anhydride, b. p. 113—120°/10 mm., and acetonylsuccinic anhydride, b. p. 200—210°/10 mm., as colourless oils. The former was identified by conversion into the anilic acid (white crystalline powder, m. p. 156°; Kohler and Butler, *J. Amer. Chem. Soc.*, 1926, **48**, give m. p. 147°. Found : C, 63.55; H, 6.1. Calc. for $C_{11}H_{13}O_3N$: C, 63.3; H, 6.3%) and into methylsuccinic acid (colourless prisms, m. p. and mixed m. p. 111°; equiv., 66); the acetonylsuccinic anhydride, which could not be induced to crystallise, or give a semicarbazone, a nitrophenylhydrazone, or a crystalline specimen of its acid (Emery, *J. pr. Chem.*, 1896, **53**, 305, describes the anhydride and the acid as solids melting at 95° and 107—109° respectively), was identified by conversion into tricarballylic acid (m. p. and mixed m. p. 160°). This conversion was accomplished by the action of potassium hypobromite, the tricarballylic acid being precipitated as the lead salt and regenerated by means of hydrogen sulphide.

Addition of Ethyl Malonate to Ethyl β-Methylsorbate.—Ethyl β-methylsorbate. The preparation of this substance in pure condition and good yield is difficult. Our experiments showed that, in the usual method of preparation from ethylideneacetone and ethyl bromoacetate (compare Burton and Ingold, J., 1929, 2029), (1) it is not advantageous to employ excess of the ketone in the preliminary Reformatski reaction, and (2) of the numerous methods which have been applied to dehydration of Reformatski products, the action

of thionyl chloride is preferable in this instance. The hydroxy-ester (85 g.) (ethyl β-hydroxy-β-methyl-Δ^{γ}-hexenoate) is dissolved in pyridine (40 g.), and into the solution, cooled in a freezing mixture, thionyl chloride (35.4 c. c.) is dropped slowly with shaking; the product is kept at room temperature for 3 hours, then poured into water, and worked up in the usual way. The conjugated ester, b. p. 115—116°/36 mm., is thus obtained in 64% yield (Found: C, 63.7; H, 8.9. Calc. for $C_9H_{14}O_2$: C, 63.6; H, 9.1%).

The additive reaction. Ethyl malonate (50 g.) was added to a solution of sodium (0.5 g) in ethyl alcohol (7 c. c.). Ether (about 10 c. c.) and the conjugated ester (23 g.) were then added, and the mixture heated in a steam-bath for 7 hours. The reaction product, worked up in the usual way, gave unchanged reactants and a colourless oil, b. p. 170—175°/10 mm. The latter proved to be a mixture of *ethyl β-methyl-Δ^{γ}-hexenoate-β-malonate* and *ethyl $\beta\delta$-dimethyl-Δ^{β}-pentene-$\alpha\varepsilon\varepsilon$-tricarboxylate* (Found: C, 61.0; H, 8.3. $C_{16}H_{26}O_6$ requires C, 61.1; H, 8.3%). Yield, 39—42%. The reduction of this mixture (in the presence of colloidal palladium or platinum) was attempted, but at room temperature only very small amounts of hydrogen were absorbed under 1 or 2 atm.

Ozonolysis of the addition product. The operation was conducted as previously described. The addition product (36 g.) gave a very viscous ozonide which decomposed to form acetaldehyde (dimethone m. p. 139°) and a mixture of aldehydic esters. The latter, which gave the expected deep colour with ferric chloride due to the presence of acetocetic ester, were further oxidised with hydrogen peroxide (see above) and subsequently hydrolysed with alkali and decarboxylated by boiling with 20% hydrochloric acid for 12 hours (direct hydrolysis with hydrochloric acid caused gross decomposition through charring). From the hydrolysis product an acid syrup was obtained which was immediately converted by acetyl chloride into a mixture of anhydrides. This distilled,

with the exception of a few drops of high-boiling material, at 115—120°/10 mm. and consisted almost entirely of methylsuccinic anhydride. The anhydride was converted into methylsuccinic acid (m. p. and mixed m. p 111°), the total yield being 9.4 g. (62% yield); no β-methyltricarballylic acid derived form an ∝β-addition product was isolated, and repetition of this experiment, with careful examination of the methylsuccinic acid, failed to establish the presence of the former acid.

The ∝β,∝δ-Ratio of the Addition Products from Ethyl Cyanoacetate and Ethyl γ-Methylsorbate.—The method previously employed in attempting to determine the composition of the addition product from ethyl γ-methylsorbate (Farmer and Mehta, *loc. cit.*) was modified as described in (*a*) and (*b*) below. By this means independent approximate estimates of the ∝β, ∝δ-ratio were obtained.

(*a*) The addition product, b. p. 190—195°/18 mm. (20 g.), was dissolved in concentrated sulphuric acid (50 g.) and kept over-night. The solution was diluted with water (120 c. c.) and then refluxed for 9 hours on a sand-bath. The hydrolysis product, a mixture of βγ-dimethyl-Δ^{γ}-pentene-∝ε-dicarboxylic acid and β-*iso*butenylglutaric acid, was extracted with ether and worked up in the usual way. Yield 90%. This acid mixture was ozonised, and the ozonide decomposed as previously described. The decomposition products were extracted with ether and distilled, giving (1) β-methyllævulic acid (2 g.), b. p. 140—150°/20 mm., and (2) the dilactone of β-acetylglutaric acid (7 g.), b. p. 200—210°/20 mm., (compare Farmer and Mehta, *loc. cit*, p. 1615). The proportions of these substances corresponded to the presence initially of 25·5% of the ∝δ-and 74·5% of the ∝β-addition product. On this basis the total yield of the pure decomposition products was 64·3%.

(*b*) Ozonolytic decomposition of the original addition product (15 g.) was carried out as described above. The subsequent procedure differed from that formerly employed

by the authors (*loc. cit.*) in that the ketonic esters first produced (ethyl α-cyano-β-methyllævulate from the $\alpha\delta$-and ethyl α-cyano-β-acetylglutarate from the $\alpha\beta$-addition product) were not converted for purposes of estimation into substances (1) and (2) [see (*a*) above] respectively. The esters differed sufficiently in b. p. from one another and from the original addition product to allow of reasonably good fractionation. It being assumed that these fractions were homogeneous, the $\alpha\beta$, $\alpha\delta$-ratio of the original addition products was 7 : 3; on this basis the yield of isolated decomposition products was 76%. The ketonic esters were subsequently shown to be respectively convertible into the acid and dilactone named above.

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Imperial College of Science and Technolgy,
London, S. W, 7

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XXIX.—Properties of Conjugated Compounds. Part XIII. The Michael Reaction and the Manner of Formation of Certain Saturated Double-addition Products.

By Ernest Harold Farmer and Thakorbhai Naranji Mehta

As a consequence of the authors' demonstration that a plural mode of attachment of ester-addenda to butadienoid compounds could obtain (J., 1930, 1610), it seemed probable that a detailed study of the course followed by the Michael and other allied reactions which proceed in alkaline solution could ultimately give unequivocal information as to the order of events in these reactions and consequently as to the mechanism of an important type of unsymmetrical addition and the manner of polarisation of conjugated esters. If, during addition, the anionic component of the addendum were the first to become attached, the resulting system could be prototropic (A) or non-tautomeric (B):

$$\begin{array}{ll} \mathrm{R{\cdot}CH{\cdot}\overbrace{\underset{\displaystyle|}{CH}{\cdot}\underset{-}{CH}{:}CH}{\cdot}CO_2R'} & \mathrm{R{\cdot}CH{:}CH{\cdot}\underset{\displaystyle|}{CH}{\cdot}\underset{-}{CH}{\cdot}CO_2R'} \\ \text{(A)} \qquad \mathrm{CH(CO_2R')_2} & \qquad\qquad \mathrm{CH(CO_2R')_2} \quad \text{(B)} \end{array}$$

in the former case the completion of addition could yield a Δ^{α}- or Δ^{β}-form of an $\alpha\delta$-addition product (in most cases, probably, the latter almost exclusively in view of the relative activating tendencies of the graoups attached to the prototropic system) and in the latter case an ordinary $\alpha\beta$-addition product. This means that the complex anions necessarily formed intermediately could not be in equilibrium with one another, so that there is no possibility of $\alpha\beta$, $\alpha\delta$-isomerisation except *via* the retrograde Michael reaction, thus: $\alpha\beta$-Product $\rightleftarrows$ Reactants $\rightleftarrows$ $\alpha\delta$-Product. If, on the other hand, the kationic component first became attached, the resulting system would be anionotropic,

$$\mathrm{R{\cdot}\overbrace{CH{:}CH{\cdot}\underset{+}{CH}}{\cdot}CH_2{\cdot}CO_2R} \qquad \mathrm{R{\cdot}\overbrace{\underset{+}{CH}{\cdot}CH{:}CH}{\cdot}CH_2{\cdot}CO_2R}$$

so that a direct mechanism for the production of isomeric forms akin to the mechanism of bromination would be provided. Both views have been put forward in connexion with the addition of unsymmetrical addenda to mono-olefinic esters nitriles and ketones. It is important to note, however, that if the initiation of $\alpha\delta$-ester addition to butadienoid compounds is dependent on the appearance of positive polarity on the δ-carbon atom of the butadiene chain, then polarisation of the Thiele type is effectively produced before reaction commences.

In the preceding paper consideration has been given to the ratio in which $\alpha\beta$- and $\alpha\delta$-addition products are formed from various butadienoid esters and ketones: the results which have been obtained do not give clear and definite support to the view that an anionotropic mechanism determines the additive mode. There is, however, a series of observations on record which seem to indicate that a consideration other than the simple ones outlined above may

enter into the problem relating to the formation of ester (and allied) addition products.

It was shown by Bechert (*J. pr. Chem.*, 1894, **50**, 13) and Hinrichsen (*Annalen*, 1904 **336**, 339) that cinnamaldehyde reacts with cyanoacetic ester and with malononitrile in the presence of a few drops of alcoholic sodium ethoxide to yield cinnamylidenecyanoacetic ester, $Ph\cdot CH{:}CH\cdot CH{:}C(CN)\cdot CO_2R$, and cinnamylidenemalononitrile, $Ph\cdot CH{:}CH\cdot CH{:}C(CN)_2$, respectively; later it was shown by Meerwein (*Annalen*, 1908, **358**, 71) that cinnamaldehyde condenses with methyl malonate in the presence of a molecular proportion of sodium methoxide to yield a saturated trimalono-compound which could reasonably be represented as the double-addition product (I) of

$$Ph\cdot CHX\cdot CH_2\cdot CHX\cdot CH(CO_2R)_2 \quad \text{(I.)}$$

$$\begin{array}{l} Ph\cdot CH\cdot CH_2 - CH\cdot CH_2\cdot CO_2H \\ \quad\;\; | \qquad\qquad\quad\; | \\ \quad CH_2\cdot CO_2H \;\; CH_2\cdot CO_2H \end{array} \quad \text{(IV.)}$$

$$Ph\cdot CH{:}CH\cdot CHX\cdot CH(CO_2R)_2 \quad \text{(II.)}$$

$$CH_2<\begin{matrix} CHPh-CH_2 \\ CO - - CH_2 \end{matrix}>CH\cdot CH_2\cdot CO_2H \quad \text{(V.)}$$

$$Ph\cdot CHX\cdot CH{:}CH\cdot CH(CO_2R)_2 \quad \text{(III)}$$

$$[X = CH(CO_2Et)_2]$$

$$Ph\cdot CH_2\cdot CHX\cdot CHX\cdot CH(CO_2Et)_2 \quad \text{(VI.)}$$

cinnamylidenemalonic ester, $Ph\cdot CH{:}CH\cdot CH{:}C(CO_2R)_2$. The tendency to the formation of this compound was so great that even when strictly molecular amounts of the reactants were employed it still appeared—mixed with unchanged cinnamaldehyde but unaccompanied by isolable amounts of cinnamylidenemalonic ester or either of the simple addition products thereof (II and III). The constitution assigned to the saturated addition product rested on its hydrolysis to a tribasic acid represented as (IV), which in turn was convertible by the action of sodium on its ester, followed by hydrolysis, into a cyclic keto-acid represented as (V).

Now the formation of a double-addition product of this kind could be explained by assuming the steps: (1) the

formation of cinnamylidenemalonic ester, (2) the formation of an $\alpha\delta$-addition product (III) which subsequently suffered $\beta\gamma$, $\alpha\beta$-double bond displacement, and (3) the addition of another molecule of malonic easter at the $\alpha\beta$-double bond of the resulting compound (compare Meerwein, *loc. cit.*, p. 338). The correctness of this view was, however, at least open to doubt, for although a simple ester-addition product of cinnamylidenemalonic ester had never been obtained[1] (consequently the possibility of realising the postulated $\alpha\delta$-addition had not been tested), yet there was evidence to show that in the paralled reaction with potassium cyanide the same conjugated ester yielded first an $\alpha\beta$-addition product, $Ph{\cdot}CH{:}CH{\cdot}CH(CN){\cdot}CH(CO_2Et)_2$, and then a saturated double-addition product representable as

$$Ph{\cdot}CH(CN){\cdot}CH_2{\cdot}CH(CN){\cdot}CH(CO_2Et)_2$$

(Thiele and Meisenheimer, *Annalen*, 1899, **306**, 252). It the monoaddition product in the latter instance were indeed wholly of $\alpha\beta$-type, then the representation of additive mode as determined by mobile ion tautomerism (of either type) in the simple manner envisaged above would become impossible of acceptance so far as ester addition is concerned. Although it is by no means certain from the published evidence that the $\alpha\beta$-hydrocyanide referred to was unaccompanied by an isomeric $\alpha\delta$-product, or that the corresponding double-addition product was unaccompanied by one or both forms of the mono-addition product, there was, however, another possibility to consider, *viz.*, the formula reasonably assigned to the doubleaddition product was incorrect and ought to be replaced by the only alternative formula (VI) which could correspond with Meerwein's observations A substance of this formula would of course give *cyclo*pentanone- instead of *cyclo*hexanone-derivatives on cyclisation, but its formation would be dependent on the occurrence of rearrangement of

[1] There is little doubt that Knoevenagel and Herz's alleged cinnamylidene*di*malonic ester, prepared by condensation of cinnamaldehyde and malonic ester in the presence of piperidine (*Ber.*, 1904, 37, 4483), was actually cinnamylidenemalonic ester (Meerwein, *loc. cit.*, p. 336).

the first-formed $\alpha\beta$-addition product whereby the malonic ester group became transferred to the γ-carbon atom.

As the manner of hydrogen cyanide addition to cinnamylidenemalonic ester and other conjugated compounds was already under investigation in connexion with another series of experiments, the authors thought it advisable to examine the reactivity of crotonaldehyde towards malonic ester. The formation of crotonylidenemalonic ester under the condensing action of piperidine had been effected by Meerwein (*loc. cit.*), but the preparation of crotonylidene-*di*malonic ester (VII) had not been accomplished. Farmer and Healey had unsuccessfully attempted to prepare the latter compound and the corresponding cyanoacetic ester addition product by addition to crotonylidenemalonic ester (J., 1927, 1065), and the present authors in renewing these attempts have found that, although some condensation can be effected between crotonaldehyde and malonic ester in the presence of a few drops of sodium ethoxide solution, the product is complex and cannot be satisfactorily fractionated; on the other hand, they have found that the interaction of the two substances in the presence of a molecular proportion of sodium ethoxide yields very readily an analogue (VIII) of Meerwein's double-addition compound (I). The behaviour of this substance (which appeared to be quite from crotonylidene*di*malonic ester or its $\alpha\delta$-isomeride) paralleled that of Meerwein's compound. It yielded by hydrolysis a tribasic acid (IX), and to some extent a cyclised derivative thereof. The latter compound (X) was also obtained by submitting the ester of (VIII) to the Dieckmann reaction and hydrolysing the solid ketonic ester so obtained, to which one of the formulæ (XI) and (XII) should apply.

$CH_3{\cdot}CH{:}CH{\cdot}CHX{\cdot}CH(CO_2Et)_2$ (VII.)

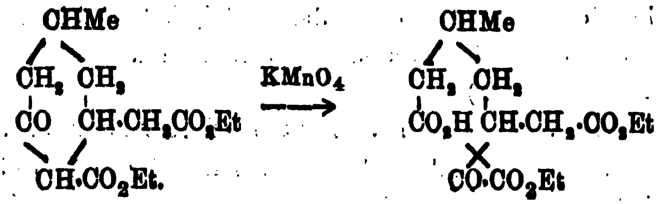
$CH_3{\cdot}CHX{\cdot}CH_2{\cdot}CHX{\cdot}CH(CO_2Et)_2$ (VIII.)

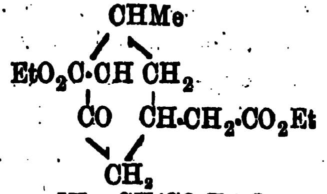
$$\begin{array}{l} CH_3{\cdot}CH{\cdot}CH_2{-}CH{\cdot}CH_2{\cdot}CO_2H \\ \quad\;\; | \qquad\qquad\; | \\ \quad CH_2{\cdot}CO_2H\;\; CH_2{\cdot}CO_2H \end{array}$$

(IX.)

$$CH_2{<}\begin{matrix} CHMe{-}CH_2 \\ CO{-}{-}{-}CH_2 \end{matrix}{>}CH{\cdot}CH_2{\cdot}CO_2H$$

(X.)

(XI.) 

(XII.) 

$[X = CH(CO_2Et)_2]$

Actually the former formula was correct, since the Dieckmann reaction product gave β-methylglutaric acid and oxalic acid as the final products of oxidation with permanganate; it followed also from the fact that β-methylglutaric acid was obtained that the formula (VI), as representing the original double-addition product, was finally confirmed, since the Dieckmann reaction product from (VII) should have yielded ethylsuccinic acid.

The formation of the saturated double-addition compound from crotonaldehyde and malonic ester thus constitutes the third known example of this type of additive reaction. Preliminary experiments on the addition of malonic ester to sorbic ester in the presence of a molecular proportion of sodium ethoxide indicate that a saturated double-addition compound is formed in this example also. It seems clear, therefore, that although reaction can proceed direct from aldehyde to double-addition product in one operation, it need not necessarily do so, but can start from the butadiene ester; in all cases, however, the employment of the sodium enolate of the addendum is necessary. It is a remarkable fact that in the formation of double-addition compounds from both cinnamylidene- and crotonylidenemalonic ester it has not been possible to arrest reaction at the stage intermediate between the formation of the butadiene ester and the double-addition compound. (In all of the numerous addi-

tions to butadiene esters under "catalytic" conditions which have been studied, reaction appears to cease at the stage of simple addition).

The conditions and manner of formation of double-addition compounds will be further investigated, but there is little doubt that *radical-migration plays no part* in their production. Therefore, since there is no appearance that the proportions in which $\alpha\beta$- and $\alpha\delta$-addition products are formed are purely fortuitous, the experimental evidence in favour of butadienoid polarisation of a conjugative type is strengthened in direct proportion as the evidence of an anionotropic relationship between isomeric addition products is weakened.

EXPERIMENTAL.

Condensation of Ethyl Malonate with Crotonaldehyde.—(*a*) *With a fractional molecular proportion of sodium ethoxide at* 0°. Condensation under these conditions proceeded to some extent, but the condensation product was obviously not homogeneous and could not satisfactorily be resolved into its component compounds by fractional distillation.

(b) *With a molecular proportion of sodium ethoxide.* Freshly distilled crotonaldehyde (98 g.; 1 mol.) and ethyl malonate (192 g.; 3 mols.) were mixed and cooled in a freezing-mixture. A solution of sodium ethoxide (9·2 g. of sodium in 140 c. c. of absolute alcohol) was gradually added during 1 hour, the temperature not being allowed to rise. The solution, which had become yellow and viscous, was kept for 3 hours at room temperature and then diluted with a large quantity of water. The alkaline liquor was extracted with ether to remove the neutral products of reaction: these consisted of unchanged ethyl malonate and a very small quantity (too small to allow of identification) of an oil, b. p. 140—150°/13 mm. The mother-liquor, after acidification with the calculated quantity of hydrochloric acid, yielded an acidic reaction product on extraction with ether. This substance, obtained as a colourless viscous liquid, was

immediately hydrolysed by boiling with 35% hydrochloric acid for 30 hours. The acid obtained by extracting the product with ether was a thick viscous oil which began to solidify after standing for some days in a vacuum desiccator and became completely solid after being kept for 3 months with occasional scratching of the containing vessel and trituration with common organic solvents. In later experiments it was found advantageous to esterify the hydrolysed product directly by dissolving it in alcohol and saturating the solution with dry hydrogen chloride; the oily product obtained could then be easily separated into two compounds, (i) a colourless oil, b. p. 140°/11 mm., and (ii) a colourless oil, b. p. 187—188°/11 mm. The former of these was *ethyl 1-methyl*cyclo*hexan-3-one-5-acetate*, which was later obtained (see below) in a different way; it yielded a *semicarbazone* (colourless prisms, m. p. 152°, from ethyl acetate. Found: C, 56·3; H, 8·2. $C_{12}H_{21}O_3N_3$ requires C, 56·4; H, 8·3%). The latter compound was *ethyl β-methylpimelate-β'-acetate* (Found: C, 61·0; H, 8·7. $C_{16}H_{28}O_6$ requires C, 60·7; H, 8·9%), which yielded on hydrolysis with hydrochloric acid pure *β-methylpimelic-β'acetic acid* in almost quantitative yield. The acid was obtained in colourless cubes, m. p. 130°, after crystallising in turn from ether-petroleum and acetone–chloroform (Found: equiv., 77. Calc: equiv., 77·3), and from the acid the corresponding crude anhydride was obtained as a non-solidifiable liquid by boiling with acetyl chloride. By saturating an alcoholic solution of the acid with hydrogen chloride at 0°, ethyl β-methylpimelate-β'-acetate was regenerated in very pure condition (Found: C, 60·5; H, 8·7%).

*Ethyl 1-Methyl*cyclo*hexan-3-one-4-carboxylate-5-acetate* — Sodium (6·2 g.) was pulverised under xylene, and the xylene replaced by benzene. To the suspension, ethyl β-methylpimelate-β'-acetate (42 g.) was added, and the mixture heated to 90° in an oil-bath. A vigorous reaction ensued which was completed by heating the product for 5 hours at 100°. The jelly-like sodium derivative was decomposed with ice-cold 10% sulphuric acid, and the derived ester extracted

with ether. The ether-benzene liquor, freed from a small amount of acidic material by shaking with sodium carbonate, was dried and distilled. It yielded pure *ethyl 1-methylcyclohexan-3-one-4-carboxylate-5-acetate* as a colourless oil, b. p. 170—172°/11 mm., which solidified after several days and gave colourless needles, m. p. 47°, on recrystallisation from light petroleum (Found: C, 62·1; H, 8·3. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·2%). Yield, 75%. No semicarbazone of this strongly enolic substance could be obtained; the *phenylhydrazone* crystallised from alcohol in long needles, m. p. 111° (Found: C, 66·5; H, 7·8. $C_{20}H_{28}O_4N_2$ requires C, 66·6; H, 7·8%, but decomposed on keeping.

1-*Methylcyclohexan-3-one-5-acetic Acid*.—Ethyl 1-methylcyclohexan-3-one-4-carboxylate-5-acetate was boiled with equal volumes of alcohol, hydrochloric acid, and water for 3 hours, the free alcohol was then expelled, and hydrolysis continued for 12 hours. The product was neutralised and traces of residual neutral material were removed by extraction with ether. From the alkaline liquor an oil was isolated which solidified after distillation (b. p. 185°/9 mm.). This crystallised in long colourless needles, m. p. 77°, from petroleum (Found: C, 63·7; H, 8·1. $C_9H_{14}O_3$ requires C, 63·5; H, 8·2%). The corresponding *silver* salt was obtained as a white powder (Found: Ag, 39·1. $C_9H_{13}O_3Ag$ requires Ag, 39·0%), the *semicarbazone* separated from methyl alcohol as a white crystalline powder m. p. 218° (Found: C, 52·6; H, 7·5. $C_{10}H_{17}O_3N_3$ requires C, 52·8; H, 7·5%); the ester obtained by warming the silver salt with alcoholic ethyl iodide was a colourless oil, b. p. 144°/13 mm., obviously identical with the above-described ethyl 1-methylcyclohexan-3-one-5-acetate (Found: C, 66·5; H, 9·1. $C_{11}H_{18}O_3$ requires C, 66·6; H, 9·15%), since it yielded a semicarbazone, m. p. 152°, identical with that previously obtained (Found: C, 56·3; H, 8·3%).

Oxidation of Ethyl 1-Methylcyclohexan-3-one-4-Carboxylate-5-acetate.—To an ice-cold suspension of the ester in very dilute aqueous caustic potash, 3% permanganate solution

equivalent to 7 atoms of oxygen was slowly added, with rapid stirring. The solution was kept over-night and then the small amount of residual permanganate was reduced by addition of a little hydrogen peroxide. After removal of the manganese mud, the solution was concentrated, acidified, and extracted with ether; the residue left on evaporation of the mother-liquor to dryness was also extracted with ether. The first ethereal extract yielded a water-soluble oily acid, partial solidifiation of which set in after inoculation with a crystal of β-methylglutaric acid. This solid portion was drained on a porous tile, and the dry solid extracted in turn with benzene, chloroform, and ether. The The benzene extract yielded crystals of β-methylglutaric acid which after recrystallising in turn from benzene and ether-petroleum melted at 87°, and did not depress the melting point of an authentic sample of the acid. The chloroform contained an acid which was extremely difficult to recrystallise, but this on further oxidation with permanganate yielded β-methylglutaric acid. The ethereal extract on concentration deposited crystals of oxalic acid, but a much larger quantity of the same acid was obtained on evaporating the ethereal extract of the solid residue (above). It was found that chromic acid yielded gummy oxidation products differing greatly from those here described.

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The Imperial College of Science and Technology,
London, S. W. 7.

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XXX—Chimie Physique.—Couleur et comportement chimique dans la serie cinnamique. Note (1)

DE Mme RAMART-LUCAS et M. TRIVEDI.

L'un de nous a insisté sur ce que le comportement chimique (énergies et vitesses de réaction) d'un chromophore, introduit dans un carbure saturé, doit changer en même

temps que l'état interne du chromophore, et par suite, en même temps que la couleur introduite par ce chromophore; et sur ce que, quand cet état interne reste le même (la couleur étant donc la même), les énergies de réaction du chromophore A sur un autre groupe B porté par une autre molécule doivent être les mêmes. ainsi que probablement les vitesses de reaction (sauf gêne stérique apportée éventuellement par enroulement dans le cas de trés longues chaines). En particulier, puisque dans une série homologue telle que H. A, CH^3. A, CH^3. CH^2. A, etc. la couleur ne change pratiquement plus à partir du troisiéme terme (ce qui veut dire que A est de moins en moins altèrè par l'allongement de la chaîne) le comportement chimique, en ce qui regardo A, sera pratiquement le même à partir du troisiéme terme ([2]). Plus généralement et en abrégé: quand un chromophore A introduit une même couleur dans diverses molécules par ailleurs absolument quelconques, elle doit avoir même comportement chimique par rapport à un groupe B fixé sue une autre molécule ([3]).

Ces prévisions se sont déjà trouvées vérifiées dans la plupart des séries homologues à chaine normale pour les réactions jusqu'ici étudiées: vitesse d'estérification des acides, de saponification des esters et des amides, vitesse de réaction des amines avec l'iodure d'allyle et avec le malonate d'éthyle, vitesse d'oximation des cétones CH·CO·(CH)·CH, etc.

Soit maintenant une molécule possédant *plusieurs chromophores liés directement*: A, B, C, D; ils exercent une influence mutuelle qui contribue de facon parfois trés importante à déterminer leur état intérieur. Si nous fixons un groupe T sur A par exemple, l'état de ce dernier changera, il en resultera une modification du ((couplage)) de A et B, par suite l'état intérieur de B ne sera plus le méme, ce qui aura pour conséquence une variation du ((couplage)) de B et C, etc. En sorte que l'on peut prévoir que l'introduction de T

([1]) Séance du 2 novembre 1932.

([2]) Mme Ramart, *Comptes rendus*, **194**, 1932, p. 726.

([3]) Mme Ramart, *Bull. Soc. chim.*, 4e série, **51**, 1932, p. 343.

sur A aura pour effet non seulement de changer l'état intérieur de ce dernier, mais aussi celui des autres chromophores.

Considérons l'acide cinnamique $C^6H^5.CH=CH.COOH$ ou l'un de ses dérivés. D'aprés ce qui précède toute substitution sur l'un des chromophores, qui aura pour effet d'en modifier l'état intérieur, doit aussi changer l'absorption et le comportement chimique des autres puisqu'ils s'influencent tous mutuellement. Nous avons étudié l'absorption des acides, esters, amides méthylcinnamiques et la réactivité des groupes fonctionnels acide, amide, ester. Nous avons constaté que l'introduction soit en position α, soit en position β-d'un groupe CH^3 (qui n'introduit par lui-même aucune couleur) change à la fois notablement et l'absorption de la molécule et la réactivité du group fonctionnel : acide, ester ou amide.

Le spectre d'absorption de l'acide cinnamique (et de ses dérivés ester, amide) est formé de deux fortes bandes: le maximum de la première est situé vers $\lambda = 2680$ $\log \Sigma = 4{,}25$, la seconde se prolonge dans l'ultraviolet plus lointain.

L'expérience nous a montré que si l'on compare l'absorption des dérivés cinnamiques et celle de leurs dérivés méthylés, on observe, pour ces derniers, à la fois une diminution de l'intensité d'absorption et un déplacement des bandes vers l'ultraviolet. En sorte que la modification de couleur se traduit par une diminution de l'absorption générale. Le phénoméne s'accentue quand on passe du dérivé cinnamique à l'α-méthyl puis au β-méthyl et enfin au dérivé diméthylcinnamique.

D'autre part, nous avons constaté que, pour tout dérivé méthylcinnamique la réactivité chimique est notablement plus faible que celle du dérivé non substitué correspondant,

Les quantités d'ester formées en chauffant les acides avec de l'alcool absolu en tubes scellés (sans catalyseur) pendant 8 heures à 100° sont indiquées dans la colonne I. Les proportions d'ester et d'amide hydrolysés par chauffage en tubes

scellés à 100° (pendant 4 heures pour les premiers et 4 heures et demie pour les seconds) avec de l'alcool contenant 0,05 molecule de HCl au litre se trouvent dans les colonnes II et III.

Dérivés:	I. (Pour 100 d'acide éthérifié).	II. (Pour 100 d'ester hydrolysé).	III. (Pour 100 d'amide hydrolysée).
Hydrocinnamiques	22,09	47,64	37,0
Cinnamiques	14,55	36,40	30,10
β-Méthylcinnamiques	12,18	36,0	30,0
α-Méthylcinnamiques	9,37	33,0	29,4
α.β-Diméthylcinnamiques	—	28,5	—

La différence entre les vitesses de réaction très notable pour les acides est plus faible pour les esters et surtout pour les amides; mais pour ces deux séries, la présence de HCl comme catalyseur peut modifier l'allure du phénoméne.

L'influence paralysante du groupe CH^3 en position β s'explique par le fait que ce radical modifie l'état interne du groupe $C^6H^5.CH$ (on sait que $C^6H^5.CH=CH^2$, $C^6H^5.C(CH^3)=CH^2$, $C^6H^5.CH=CH.CH^2$ n'ont pas la même couleur) et par suite l'action mutuelle qui s'exerce entre les radicaux $C^6H^5.CH=CH$ et COOH (l'ester ou l'amide). Lorsque la substitution a lieu en α deux effets se superposent : l'un d'eux concerne la modification de $C^6H^5.CH=CH$ laqulle se répercute sur COOH et l'autre qui provient du couplage des groupes CH^3 et COOH qui sont fixés sur le même carbone.

En résumé : les groupes CH^3 qui par eux-mêmes sont incolores dans l'ultraviolet moyen et n'ont qu'une très faible réactivité chimique modifient notablement à la fois la couleur de la molécule et la réactivité chimique des fonctions acide, ester, amide, lorsqu'ils sont introduits dans la chaîne des dérivés cinnamiques.

« (Extrait des Comptes rendus des seances de l' Academie des Sciences, t 195, p. 783, seance du 7 novembre 1932.)

XXXI—The Principles Underlying Aromatic Side-chain Reactivity from the Standpoint of the Electronic Theory of Valency.

By Christopher Kelk Ingold and Chaturbhai Shankerbhai Patel.

1. *Historical : Principles of Correlation and Inversion.*

Recent work on the effect of nuclear substituents on reactions in the side-chains of benzene derivatives had led to generalisations which pave the way to a theory of aromatic side-chain reactivity closely linked with the modern theory of nuclear aromatic substitution.

Some time ago Olivier demonstrated the existence of a relation between nuclear and side-chain reactivity, for the example of the latter represented by the acid hydrolysis of benzene chlorides (*Rec. trav. chim.*, 1922, **41**, 301, 646; 1923, **42**, 516, 775): the velocities of hydrolysis for three isomers of ihe form $R\cdot C_6H_4\cdot CH_2Cl$ were found to be in the order *o*, *p*>*m* or *m*>*o*, *p*, according as R belonged to the *op*- or *m*-orienting series; and, moreover, the facilitating or retarding action of different groups R exhibited a close parallelism to their influence on reactivity in ordinary nuclear substitution. Similar relationships have since been established for several other side-chain transformations, including the condensations of benzyl chlorides with benzene in the presence of aluminium chloride, the saponification of benzoic esters, the addition of hydrogen sulphide to benzonitriles, and bromination in a methyl side-chain (Olivier and Berger, *ibid.*, 1926, **45**, 710; 1927, **46**, 605; Kindler, *Annalen*, 1926, **450**, 1; Ingold and Rothstein, *J. Chem. Soc.*, 1928, 1217).

It is known, however, that there is another group of side-chain reactions for which the above relations become to a large extent inverted. Lapworth, Shoesmith and others have found (*J. Chem. Soc.*, 1922, 1391; 1924, 1312, 2278; 1926,

214) that the two groups of nuclear substituents for which the ease of acid hydrolysis of isomeric benzyl halides are respectively in the order *o*, *p*>*m* and *m*>*o*, *p*, become intere changed (with the exception of chlorine and bromine—see Section 6) when the reaction studied is the reduction of benzyl bromides with hydriodic acids; indications of a similar phenomenon are apparent in the work of Franzen and Rosenberg (*J. pr. Chem.*, 1920, *ii*, **101**, 333) on the alkaline alcoholysis of benzyl halides; and Tasman has shown (*Rec. trav. chim.*, 1927, **46**, 653) that the effect of different nuclear substituents on the velocity of alkaline hydrolysis of phthalides runs antiparallel to their influence on reactivity in the side-chain transformations mentioned in the preceding paragraph. A further clear illustration is available in the work of Conant, Kirner and Hussey (*J. Amer. Chem. Soc.*, 1925, **47**, 448), and especially in that of Bennett and Berry (*J. Chem. Soc.*, 1927, 1676) on the conversion of benzyl chlorides into corresponding iodides. Obviously the two groups of side-chain reactions are in some fundamental respect the inverse of each other, and this circumstance is of course, at the basis of the successful application by Lapworth and Shoesmith of the principles of alternate polarities to most of the examples studied by them.

2 *Classification of Side-chain Reactions*

The view here under development incorporates the above analogies and conclusions, and starts from the classification of side-chain transformations given by Ingold and Rothstein (*Ann. Reports, Chem. Soc.*, 1927, **24**, 155; J. *Chem. Soc.*, 1928, 1217). These reactions are divided into two main categories according to whether (type A) an *influx* of electrons from the nucleus towards the side-chain, or (type B) a *recession* of electrons from the side-chain towards the nucles, facilitates the change. The influx of electrons which assists reactions of type A may be required either to liberate or partly liberate a portion of the side-chain which carries all its

electrons with it (type A_1) or to attract towards the side-chain an electron-seeking reagent (type A_2). Similarly, the electron-recession which facilitates reactions of type B may assist either the partial or complete liberation of a group which abandons a previously shared electron-pair (type B_1), or the electrostriction of a basic (positive-centre-seeking) reagent (type B_2). The following table contains some examples.

Type.	Example.	Facilitated process.
A_1	Thermal fission of benzylammonium hydroxides	$Ph\rightarrow Ch_2—NR_3+$
„	Acid hydrolysis of benzyl chloride	$Ph\rightarrow CH_2—Cl$
„	Addition of H_2S to benzonitrile	$Ph\rightarrow C\equiv N$
A_2	Side-chain bromination of toluene	$Ph\rightarrow CH_3\ldots\overset{\delta+}{Br}.\overset{\delta-}{Br}$
B_1	Reduction of benzyl bromide by HI	$Ph\leftarrow CH_2—Br\ldots I.H$
B_2	Alkaline alcoholysis of benzyl chloride	$Ph\leftarrow CH_2Cl\ldots\overline{OEt}$
„	Conversion of benzyl chloride into iodide	$Ph\leftarrow CH_2Cl\ldots\overline{1}$

It should be stated that, in the absence of data relating to the influence of nuclear substitution of velocity, the preliminary assignment of a side-chain reaction to its proper class is one of the main practical difficulties in the application of the theory, and that although an analysis of the circumstances of the reaction and of the type of reactivity normally characteristic of the aromatic compound and reagent is always valuable as a guide, it frequently fails to do more than indicate a probable allocation. In general, two separate points require consideration: first, a decision is required

between two alternative possible mechanisms, which are usually related much as are those of the second and sixth of the above examples; secondly, it must be decided which phase of the actual mechanism controls the speed, although naturally, if intermediate forms are not present in appreciable concentration, the rate-controlling phase is necessarily the initial one. The utility in connection with this part of the problem, of data relating to the influence of nuclear substitution on side-chain reactivity can immediately be made apparent without reference to the less superficial points which arise in the adaptation of the theory of nuclear aromatic substitution to side-chain reactions. Facilitation by a uniquely electron-repelling group (*e. g.*, *p*-Me) and retardation by a uniquely electron-attracting group (*e. g.*, *p*-NO_2) is diagnostic of reactions of type A, whilst the inverse of these effects characterises reactions of type B. Further-more, it is possible to detect complications due to simultaneous membership of both types,—a condition which may arise from two main causes; either the side-chain reaction may proceed by two contemporaneous mechanisms, one belonging to each type, or its single route may involve two rate-affecting phases, one of each type. If there are two simultaneous reactions the speeds corresponding with a reries of nuclear substituents taken in order of decreasing electron-release and increasing electron-restraint should pass through a single minimum, because at both extremes of the series the acceleration of one mechanism will mask the retardation of the other; possible examples of this effect are provided by Franzen and Rosenberg's experiments and by Berger and Olivier's investigation of the hydrolysis of benzoyl chlorides (*Rec. trav. chim.*, 1927, **46**, 516; compare *Ann. Reports, Chem. Soc.*, 1927, **24**, 157). If a single mechanism requires both electron-absorption and release, the velocities should pass through a single maximum, since at both ends of the series the retardation of one phase will mask the acceleration of the other; it has been suggested (*Ann. Reports, Chem. Soc.* 1928,

25, 147), on the basis of Lapworth and Manske's investigations (*J. Chem. Soc.*, 1928, 2533) that such conditions obtain in the formation of cyanohydrins from benzaldehydes. The matter is considered further in Section 7.

(3) *Reactions Requiring Electron-release.*

A transformation having been assigned to type A, the modern theory of ordinary nuclear benzene sustitution (for summary see *Rec. trav. chim.* 1929, **48**, 799), in which it is implicit that the substituting agents require available electrons at the focus of reaction, may be applied. Adaptation is necessary, however, in order to allow for the circumstance that the effects of nuclear substituents have to traverse not only the nucleus, but also part of the side-chain in order to reach the region of reaction. It may be recalled that Ingold and Shaw (J. *Chem.* *Soc.*, 1927, 2918) have shown how the electron-availability at a nuclear carbon atom in a mono-substituted benzene is modified by (*a*) the nature, and (*b*) the orientation, of the substituent. As to (*a*),...groups were divided into four categories, according to their electron-affinities relatively to that of the hydrogen atom they replace, and according to whether or not the groups possess unshared valency electrons, the presence of which would enable negative charges to appear in the nucleus as a result of tautomeric transformation. As to (*b*),—it was found, when the mode of propagation of effects originating in these causes was considered, that whereas the permanent electron-affinity of the group increases or decreases the electron-availability of the *o*- and *p*-carbon atom strongly, and affects the *m*-carbon atoms in the same sense but to a smaller extent (inductive effect, $\pm I$), the existence of a mechanism whereby an electromeric charge-transfer can occur when stimulated by an electron-demanding reagent augments the effective electron-availability of the *o*- and *p*-carbon atoms, but is without sensible effect on the *m*-carbon atoms (tautomeric effect, $+T$). The following table of examples is intended to

facilitate the application of these principles. The special modification which it is necessary to introduce in applying them to side-chain reactions of type A are two-fold. First, owing to the small displaceability of the electrons in a single linking, selectively heavy damping accompanies the transmission of the tautomeric effect through side-chain single-linkings to the point of reaction (compare Goss, Ingold and Wilson, J. *Chem. Soc.*, 1926, 2443; also *Rec. trav. chim.*, 1929, **48**, 804). Secondly, for a reason explained below, the tautomeric effects should, with additional damping in the nucleus, affect reactivity in *m*-side-chains.

Classification A *of Nuclear Substituents*

($+I$, *op*->*m*-activation. $-I$, *op*->*m*-de-activation.
$+T$, *op*-activation).

Group No.	*Mechanism.*		*Examples.*
1.	$+I$	$\leftarrow$R	·Me, ·CMe_3
2.	$-I$	$\rightarrow$R	·CO_2H, ·COMe, SO_2R, ·NO_2, ·NMe_3
3.	$-I+T$	$\rightarrow$R	·OMe, ·Hals, ·NO, ·SOR, $\overset{+}{SMe_2}$, ·$\overset{+}{IPh}$
4.	$-I-T$	$\leftarrow$R	·CR : CR'R',' ·$\overset{-}{O}$

A comprehensive exemplification of this part of the general theory, which, it will be seen, incorporates the equivalent of Olivier's correlation principle, can be found in the work of Olivier, Berger, Kindler, Lapworth, Shoesmith and others already referred to (Section 1), and detailed allusion may be omitted. Further consideration may, however, appropriately be given to the two special circumstances (above) which complicate the analogy between nuclear and side-chain reactivity, since these determine the limitations affecting the validity of Olivier's correlation principle within the field to which it was intended to apply.

4. *Limitations of the Correlation Principle.*

The effect of selective damping in the side-chain may first be considered. In group 3 of the above classification of substituents, the inductive and tautomeric effects work in opposite directions, and everything depends, therefore, on the relative importance, so far at least as concerns *op*-nuclear reactivity and type-A reactivity in *op*-side-chains. The inductive effect results in de-activation, to an extent depending on the electron-affinity of the group; the tautomeric effect leads to activation, in proportion to the tendency of the unshared electrons to become shared, that is, to the basicity of the group. Now the electron-affinity of the halogens in the neutral state is pronounced (compare stability of the halide ions), but iodine differs from the others in possessing considerable basicity (compare stability of iodinium ions); and in nuclear substitution (nitration) it has been found (Ingold and Shaw, *loc. cit.*) that for iodine, the tautomeric effect predominates, this element belonging to the *op*-activating section of the group-3 substituents, whilst, for the other halogens, the inductive effect has main importance, and these belong to the de-activating series. In type-A side-chain reactions, on the other hand, the tautomeric effect of iodine, presumably owing to selective damping, no longer outweighs the inductive, and this element ranges itself with the other halogens as a de-activating substituent. It will be seen that the iodine substituent qualitatively violates Olivier's correlation principle, and that the broader theory naturally accommodates the apparent anomaly.

Before exemplifying tautomeric polar influence on reactivity in a *m*-side-chain, a few words of explanation are desirable with regard to the theoretical inference that such effects should be perceptible. It will be readily understood how, in nuclear substitution, in which the reagent normally has the choice of exciting and thereafter utilising, the tautomeric effect in those positions (*o*- and *p*-) in which they

are primarily, and hence most easily, stimulated, the orientation process is largely self-definitive,—the reagent becoming more and more irrevocably committed to *o*- or *p*-attack during its approach, from the moment when it began to exert electrical action on the aromatic molecule until union is definitely accomplished; thus it is that the $+T$-effect (unlike the $+I$-effect which is a permanent property of the aromatic molecule) never leads to appreciable *m*-substitution. On the other hand, a reagent attacking a *m*-side-chain has no alternative method of utilising an existing mechanism for tautomeric electron displacement within the nucleus than that of allowing the final stages of transmission of the effect of such displacements to proceed to the point of reaction by ordinary induction; and thus a substituent should, by its tautomeric, as well as by its inductive, effect, influence reactivity in *m*-side-chains, although naturally to a less degree than were the side-chains otherwise situated. It is possible to perceive the operation of this principle in several recorded observations on side-chain reactions, but all are rendered more or less complicated by the simultaneous presence of the inductive effect, the relay of which to the *m*-position is not peculiar to side-chain reactions. In the experimental part of this paper, however, we show that a *m*-phenyl substituent appreciably increases the speed of acid hydrolysis of benzyl bromide. Now phenyl (a form of substituted vinyl) is a substituent of group 4 in the above classification, but its inductive effect is negligibly small; in diphenyl itself it is not merely small, but is zero, both from symmetry and from the determined zero dipole moment of this hydrocarbon. The strong *op*-orienting action of phenyl is, of course, a manifestation of its tautomeric effect. Therefore, since in the phenyl-substituted benzyl bromide the tautomeric effect alone is under observation, the experiments referred to definitely confirm the anticipated cause of failure here considered of the simple analogy with nuclear substitution.

5. *Reactions Requiring Electron-restraint.*

For side-chain reactions known to belong to type B, the procedure corresponding to that described above, utilises, not the analogy of ordinary nuclear substitution, that is the replacement of nuclear hydrogen by the action of negative-centreseeking reagents, but the analogy furnished by aromatic substitution reactions in which the replacement of electronegative elements such as chlorine is effected by the attack of positive-centre-seeking (basic) reagents. The theory of this kind of aromatic substitution has not yet been greatly developed, but it has been outlined (Ingold, *Rec. trav. chim.*, 1929, **48**, 809); and the main features are, first, that the manifestations of the inductive effect become reversed in sign, $+I$ representing deactivation and $-I$ representing de-activation and $-I$, activation, although their nuclear distribution, *op*>*m*, remains as before; and second, that whilst the tautomeric effect $+T$ is not stimulated by the reagents now under consideration an *op*-activating tautomeric effect $-T$, depending on $\alpha\beta$-unsaturation in the orienting substituent, is rendered operative by such reagents, since this structural feature permits the appearance in the nucleus of positive charges by electromeric transfer. This scheme of classification, which is illustrated in the table below, will also apply to side-chain reactions of type B, after introduction of qualifications similar to those mentioned in section 3, relating to the diminished relative importance of the tautomeric effect, and the ability of this effect to penetrate a *m*-side-chain.

Classification B *of Nuclear Substituents.*

($+I$, *op*—>*m*-de-activating. $+I$, *op*—>*m*-activating. $-T$, *op*-activating.)

Group No.		*Mechanism*	*Examples.*
1.	$+I$	$\leftarrow$R	Me, CMe_3, $\bar{O}$
2.	$-I$	$\rightarrow$R	Hals., $\overset{+}{N}Me_3$

3, $-I-T \mid \leftarrow -R$ CO_2H, NO, NO_2, CN

4. $+I-T \mid \rightarrow R$ CR:CR'R".

On comparing this scheme with that mentioned in Section 3, it becomes evident that, owing to the radically altered nature of the tautomeric effect, the influence of groups on the kinds of nuclear substitution now considered is far from being uniformly the inverse of their influence on reactivity in the replacement of nuclear hydrogen. On the other hand, in side-chain transformations, the diminished importance of the tautomeric effect, leads to a certain simplification of the theory, inasmuch as it renders the modifying influence of groups on type-B reactivity more nearly the uniform inverse of their effect on reactivity in changes of type-A. In short, a fairly consistent inversion of the kind indicated is to be expected, and It is on this basis that the theory accommodates the series of relations formerly elucidated by the principle of alternate polarities. Ample illustration of this matter is to be found in the work of Oliver, Tasman, Lapworth, Shoesmith, Conant, Bennett and others already mentioned (Section 1); at the present stage more interest attaches to expected departures from exact inversion. This is discussed in the next Section, but it is appropriate to mention here that the appended experimental record contains a proof, on similar lines to those indicated in Section 4, that the kind of tautomeric effect which is specially characteristic of side-chain reaction of type B, *can* influence reactivity in a *m*-side-chain.

6. *Limitations of the Inversion Principle.*

Failure of the inversion rule is to be expected amongst groups which are associated with a powerful tautomeric (or weak inductive) effect, and at the same time fulfil one of two conditions relating to classification. These conditions are

(1) that the group shall belong to group 3 of classification A and also to either of groups 2 or 3 of classification B, and (2) that it shall belong to either of groups 1 or 4 of the A-classification, and also to group 4 of the B-classification.

An illustration is furnished by the anomalous behaviour of chlorine and bromine mentioned in Section 1. These substituents fulfil the first of the above alternative classificatory conditions since they belong to group 3 of the type-A scheme, and group 2 of the type-B scheme. In nuclear substitution they are in the peculiar position of being de-activating but *op*-orienting; that is, their inductive effect $(-I)$ depresses reactivity throughout the nucleus, the *m*-positions included, whilst their tautomeric effect $(+T)$ restores activity to the *op*-positions only, raising them above the standard of reactivity set by the de-activated *m*-position (*op*-orientation) but not up to the standard represented by unsubstituted benzene (de-activation). In the acid hydrolysis of the chloro and bromo-benzyl bromides (type-A reaction) these phenomena qualitatively repeat themselves: the substituted compounds are all hydrolysed more slowly than benzyl bromide, but the isomerides amongst themselves stand in the order $op > m$ as regards their rates of reaction. Turning to the reduction of these compounds (type-B reaction), the tautomeric effect $(+T)$ of the nuclear substituents should be inoperative and their inductive effect $(-I)$ should activate in all positions in the normal order, $op > m$; and this is what happens. In short, when the substituted compounds are compared with the unsubstituted parent the inversion rule holds, but when the substituted isomerides are compared amongst themselves the inversion rule fails. The anomaly, although inconsistent with any simple alternating principle, is thus naturally accommodated by the view here developed.

In the appended experimental record will be found an instance illustrating the even more complete failure of the inversion principle. The nuclear substituent was chosen to

fulfil the second of the two alternative classificatory conditions, and in selecting it we had in mind, not only the further theoretical requirement that its inductive effect should be relatively small, but also the practical one that it should be inert towards the reagents employed. The latter condition ruled out many forms of the substituted vinyl group which otherwise would have been suitable. On the other hand, phenyl is a group which possesses the necessary stability and has the added advantage that its inductive effect is entirely negligible. The influence of the nuclear phenyl substituent on certain side-chain transformations was therefore investigated, and following precedent, we utilised the acid hydrolysis of benzyl bromides as representative of side-chain reactions of type-A, whilst reduction of the same compounds with hydriodic acid served to exemplify the reactions of type-B. We are able to show, first that the introduction of a phenyl group into either the *m*-or *p*-position of benzyl bromide enhances both the velocity of hydrolysis and that of reduction, and secondly, that, as regards the relative reactivities of isomerides, the *m*- and *p*-compounds retain the same order, namely $p>m$, for both reactions. The inversion principle thus fails on both counts, and it is clear that, as theoretically anticipated, whilst the phenyl group has the ability to generate tautomeric electron-displacements in either sense, the direction of the displacements actually stimulated in a given case depend on the necessities of the attacking reagent. Incidentally it may be noted that this is exactly the result which is needed to reconcile the observed effects of phenyl in another field of investigation, in which it has found that this group can excite mobility in attached tautomeric systems, not only when the displaceable atom is released as a cation (*e. g.*, H,-" prototropy ") but also when it migrates as an anion (*e. g.* Br.,- " anionotropy "); these observations necessitate the assumption of electron-absorption or-release by phenyl according to the electrical requirements of the kind of tautomerism involved (Burton, Ingold and Shoppee, J. *Chem.* Soc., 1928, 904, 1650; 1929, 447 1199).

7. *Reactions Requiring Electron-absorption and Release.*

It is necessary to refer once more to the classification of side-chain reactions which forms the starting point of the considerations here presented. The classification assumed that side-chain reactions depend on a preliminary dissociation or association, in the course of which an electric charge, appearing in the side-chain leads to consequential electrical adjustments as between the side-chain, the nucleus and any substituents attached thereto. When several aromatic nuclei possess a common side-chain a counterpart to these assumed, transient dissoacitions can be found in directly demonstrable ionic equilibria in which the charged components have considerable life (*e. g.*, Ph_3 C·K and Ph_3 C·Cl in ionising solvents): but, under the same structural conditions, another type of dissociation also becomes directly observable, in which the separable components apparently bear no charge (*i. e.*, $Ph_6 C_2 \rightleftarrows 2\ Ph_3 C$ in non-ionising solvents). A theory of side-chain reactivity obviously cannot be general unless it includes recognition of this type of dissociation also, not only when it is pronounced as in the chemistry of free radicals, but also in any of its more ephemeral manifestations, should these arise in other circumstances. The conditions leading to the stability of free radicals have been considered by Burton and Ingold *Proc. Leeds Phil.* Soc., 1929 1, 421) whose conclusions, in so far as they affect the question under discussion, may be summarised as follows: The side-chain of a free radical, although neutral, may be regarded as initially unsaturated, with respect to both negative and positive electricity, because it requires to gain or lose an electron in order to complete its duplets (achieve spin-symmetry), and to lose or gain an electronic charge in order to recover the neutrality which the completion of the duplets would destroy. Now if this interpretation of the electrostatic condition of free radicals is correct, then the essential condition for promoting dissociation into neutral

components is the possibility of *duplex* electrical re-adjustments; and if this actually is the case, a general provision for side-chain reaction depending on such a mechanism has already been made (although not hitherto explicitly) in the foregoing statement of the theory, inasmuch as reactions have been envisaged which are characterised by the inclusion within a single mechanism of " phases " (which need not necessarily be *stages* in the sense implying separation in time) respectively dependent on electron--absorption and release. Some justification for contemplating such a category of side-reactions is to be found in the fact that the inferred practical criterion relating to the effect of nuclear substituents has been experimentally encountered (Section 2) but the investigation referred to did not include a study of the phenyl substituent, the duplex tautomeric effect of which should place it in a highly peculiar position with respect to such reactions. In this conclusion one may perceive a reason why the sufficient accumulation of phenyl, or other aryl groups possessing a common side-chain constitutes almost the only known structural condition for the realisation of considerable dissociation into neutral components; furthermore the obvious corollary that the introduction of phenyl substituents into any positions (but especially into the *o*-or *p*-positions) of the aromatic nuclei bearing the side-chain should increase such dissociation is confirmed, so far as substitution in the *p*-position is concerned by Schlenk's well-known work on free radicals containing the *p*-diphenylyl group. Apart from the *p*-diphenylyl, however, other polynuclear aryl groups are known markedly to facilitate dissociation into radicals, and since the order of the relative intensities with which they do so is also known, a simple test of the whole matter can be made.

The work of Schlenk and Gomberg and their collaborators (*Annalen*, 1910, **372**, 1; *J. Amer. Chem. Soc.*, 1917, **39**, 1652; 1922, **44**, 1829) establishes the sequence—

α-naphthyl>β-naphthyl>*p*-diphenylyl>phenyl

for the ability of these groups to promote dissociation into neutral radicals. If this sequence is to be interpreted as representing capacity for the duplex electrical readjustments reffered to above, then the same series should represent in addition, firstly, the order in which the groups facilitate side-chain reactions involving dissociations dependent on electron-release (reactions of sub-type A_1), and secondly, the relative facilitation by the groups of side-chain transformations dependent on dissociations demanding electron-restraint (reactions of sub-type B_1). The reactions we have studied belong respectively to these sub-types; and for both reactions we find a sequence identical with the above :

α-naphthyl>β-naphthyl>*p*-diphenylyl>*m*-diphenylyl>phenyl

It is scarcely necessary to add that completeness is not claimed for theoretical treatment here outlined. In particular, separate discussion is required regarding two other structural influences, namely, those due to external molecular electric fields, and to steric factors, which become of considerable importance in certain cases of *o*-substitution.

EXPERIMENTAL.

1. *Preparation of Aryl Methyl Bromides.*

3-*Bromomethyldiphenyl.*—3-Methyldiphenyl was prepared by a method identical in principle with that of Perrier (*Bull. Soc. Chim.*, 1892, [3], 7, 181) and purified by alternate fractionation (column) and freezing. Bromination was effected by leading dry bromine (10% excess) into the hydrocarbon at 200° (bath temperature) and fractionating the product. The pale yellow oil, b. p. 150°/ 15 mm., consisted essentially of 3-bromomethyldiphenyl contaminated by an inert impurity not containing side-chain bromine. Therefore, as preliminary to the quantitative work described below, the percentage purity of each sample was determined by treatment with alcoholic trimethylamine and estimation of the ionic bromine

thus formed. m-*Phenylbenzyltrimethylammonium picrate*, obtained by addition of aqueous sodium picrate to a solution of the quaternary ammonium bromide prepared in this way, separated from aqueous alcohol in rhombic plates, m. p. 152°, (Found: C, 58·2; H, 4·79. $C_{22}H_{22}O_7N_4$ requires C, 58·15; H, 4·85 per cent.).

4-*Bromomethyldiphenyl.* —4-Methyldiphenyl was prepared (compare Carnelly, J. *Chem. Soc.*, 1876, **29**, 13), purified, and brominated as in the former example, and the bromination product fractionated. The portion, b. p. 130-140°/10 mm., which solidified on cooling, yielded 4-*bromomethyldiphenyl* as pearly leaflets, m.p. 82°, on crystallising from a mixture of ether and ligroin below 0°. (Found: C, 63·3; H, 4·36. $C_{13}H_{11}Br$ requires C, 63·2; H, 4·45 per cent.). The substance gave the theoretical proportion of bromide ion when treated with trimethylamine by the method illustrated for the -*m*compound and the quaternary ammonium bromide solution, when treated with aqueous sodium picrate, yielded p-*phenylbenzyltrimethylammonium picrate*, which crystallised from aqueous alcohol, in rhombic plates, m.p. 179°. (Found: C, 57·9; H, 5·11. $C_{22}H_{22}O_7N_4$ requires C, 58·15; H, 4·85 per cent.). The less volatile portion of the bromination product on crystallisation from alcohol, with use of charcoal, yielded a yellow microcrystalline powder, m. p. 129°. Analysis showed this to be a *dibromo-4-methyldiphenyl.* (Found : C, 48·0; H, 3·32. $C_{13}H_{10}Br_2$ requires C, 48·1; H, 3·07 per cent). Except that its stability to boiling alcohol indicates that both bromine atoms are attached to the uncleus, there is no evidence of their orientation, but the most probable positions would appear to be the 2 : 4'-positions.

∝-*Bromomethylnaphthalene.*—This was prepared as described by Schmidlin and Massini (*Ber.*, 1909, **42** 2389), but we confirm Shoesmith and Rubli's statement (*J. Chem. Soc.* 1927, 3098) that it is a crystalline solid, m. p. 53°.

β-*Bromomethylnaphthalene.*—The compound, which had the properties recorded by Schultz (*Ber.*, 1884, **17**, 1529),

was prepared by his method, except that the temperature during bromination was maintained at 20°.

2. *Hydrolysis of Aryl Methyl Bromides.*

General Method.—Weighed quantities (about 0·08g.) of the bromide, each dissolved in 100 c. c. of 90% aqueous alcohol, were kept in a thermostat at 24° for various measured periods of time and the liberated hydrobromic acid titrated with carbonate-free sodium hydroxide. Usually from 20-45% of the complete reaction was followed in this way and the velocity coefficients were then calculated from each observation by means of the formula $k = (1/t) \times \log_{10} a/(a-x)$, the units of time being minutes.

Preliminary experiments with β-bromomethylnaphthalene in which the reaction was followed nearly to completion showed that its course substantially conforms to the unimolecular law although the calculated coefficients tends to fall slightly near the end of the process.

Results.—These are summarised in the following table, in which the second set of determinations relating to β-bromomethylnaphthalene is included to show that the disturbance associated with the "tail" of the reaction is without influence on the velocity coefficients recorded for the first 20-45% of hydrolysis, since, even if as much as 80% of the change is followed, the mean coefficient remains substantially the same :—

Substance hydrolysed.	Number of observations.	Percentage of reaction followed.	Calc. $k \times 10^6$ Minimum.	Maximum.	Mean.
Benzyl bromide	3	20·7	76	79	78
3-Bromomethyl. diphenyl.	6	34·3	138	154	146
4-Bromomethyl-diphenyl.	8	37·5	158	173	165
β-Bromomethyl-naphthalene.	5	45·3	170	192	184
"	10	81·5	177	195	185
α-Bromomethyl-naphthalene.	6	40·7	203	227	220

The relative values of the coefficients obtained for ∝-and β-bromomethylnaphthalene are consistent with Shoesmith and Rubli's observations on these substances (*loc. cit.*).

3 *Reduction of Aryl Methyl Bromides.*

General Method.—(*a*) Weighed quantities of each bromide (about 0·15 g.) were reduced for 1 or 2 hours at 100° in 10 c. c. of a solution prepared from constant-boiling hydriodic acid (1 vol.) and glacial acetic acid (10 vols.), and the liberated iodine estimated as usual. Simultaneously with each experiment a control was perfomed in which all conditions were maintained the same, except for the omission of the bromide, the object being to eliminate error arising from the liberation of iodine by atmospheric attack.

(*b*) Weighed quantities (about 0·3 g.) of those bromides which were found to be reduced nearly completely under the conditions of method (*a*) were each reduced at 66° for 6 or 15 hours with 10 c. c. of a solution prepared by making 1 vol. of constant-boiling hydriodic acid up to 5 vols. with glacial acetic acid. The remainder of the experiment, and the controls, were carried out as above.

Results.—These are recorded in the following table, the footnote to which illustrates the degree of consistancy of individual experiments.

Substance reduced.	Percentage reduction.			
	Method (*a*)		Method (*b*)	
	1 hour.	2 hours.	6 hours.	15 hours.
Benzyl bromide	—	32*	—	—
3-Bromomethyl-diphenyl.	26	43	—	—
4-Bromomethyl-diphenyl.	36	67	—	—
β-Bromomethyl-naphthalene.	95	99	23	41
∝ -Bromomethyl naphthalene.	96	99	35	59

* (Individual values : 32, 34, 30, 30·5%).

The results for the bromomethylnaphthalenes are not in good agreement with those obtained by Shoesmith and Rubli (*loc. cit.*)

Summary.

A theory of aromatic side-chain reactivity, linking this subject on the one hand with nuclear aromatic substitution and on the other with pure radical chemistry, is advanced and supported by observations on the reactivity in hydrogen and reduction of polynuclear analogoues of benzyl bromide.

One of us (C. S. P.) desires here to acknowledge his indebtedness to the Government of H. H. the Maharaja Gaekwar of Baroda for granting to him a period of study-leave during which this investigation has been carried out.

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The University, Leeds.

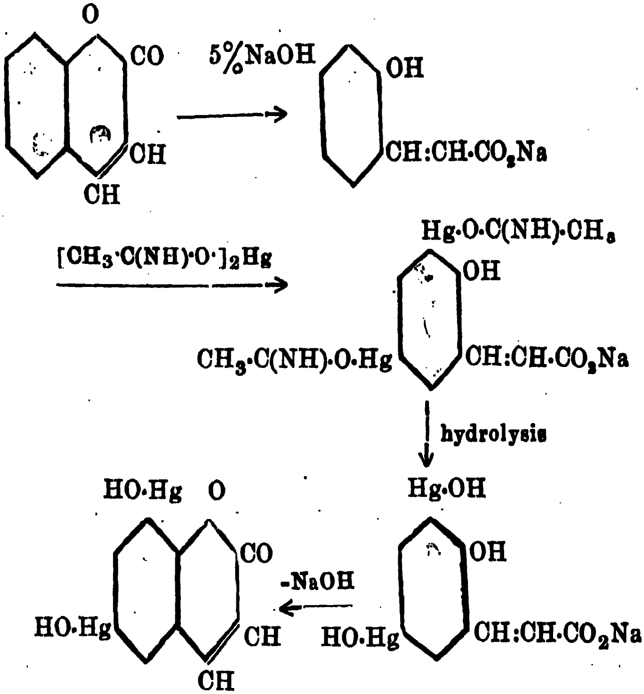
XXXII—The Influence of Substituents on the Mercuration of Coumarins.

BY KUVERJI G. NAIK AND AMBALAL D. PATEL.

Mercury acetamide, which has been used as a mercurating agent for compounds containing a reactive methylene group (Naik and Shah, *J. Indian Chem. Soc.*, 1931, **8**, 29), is effective also in the mercuration of coumarins. It does not attack these directy, but only after the action of 5% sodium hydroxide solution upon them. The course of the reaction with coumarin may be represented by the scheme given below.

Mercury acetamide has thus been made to react with the following substances (the numbers in parentheses indicate the compounds referred to in the tables): (1) coumarin, (2) 7-hydroxy-4-methyl-, (3) 7-amino-4-methyl-, (4) 4 : 7-dimethyl-, (5)5 : 6-dihydroxy-4-methyl-, (6) 6-hydroxy-4-methyl, (7) 6-nitro-, (8) 4 : 6-dimethyl-, (9) 4 : 8-dimethyl-, (10) 7-hydroxy-4 : 5-dimethyl-, (11) 7-hydroxy-4-methyl-, (12) 7-hydroxy-3-benzyl-4-methyl-, (13) 7-hydroxy-4-phenyl-, (14) 3-car-

bethoxy-, (15) 3-acetyl-, (16) 3-benzoyl-coumarin, (17) ketodicoumarin, (18) thiocoumarin, (19) 6-methyl-1 : 2-α-naphthapyrone, (20) 6-methyl-3 : 4-β-naphthapyrone. The

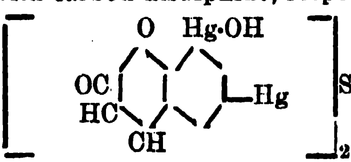


effect of substituents in the coumarin ring on their mercuration is well marked. When the oxygen of the carbonyl group is replaced by sulphur, mercuration takes place in alcoholic solution without the aid of alkali. Coumarins containing a carbethoxy or a carbomethoxy-group in position 3 give dimercury derivatives, but those containing a benzoyl group or $CO{\cdot}C_9H_5O_2$ (as in ketodicoumarin) in this position give only monomercurated compounds. Substituents in position 4 have scarcely any influence, dimercury derivatives being produced. When position 5 or 7 is occupied by a hydroxy- or an amino-group, dimercury derivatives are obtained, but 7-methylcoumarin gives a monomercury derivative only. When position 6 is substituted different

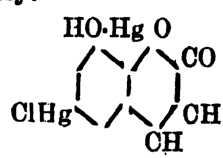
products are obtained according to the nature of the substituent: with a methyl substituent, a monomercury derivative is obtained; a nitro-substituent is expelled and a monomercury derivative produced; a hydroxy-substituent is converted into O·Hg·OH. A coumarin with methyl in position 8 yields a monomercury derivative substituted in position 6. 6-Methyl-1 : 2-α-and -3 : 4-β-naphthapyrone yield each only a monomercury derivative.

All these compounds are more or less soluble in dilute sodium hydroxide solution. The carbon-mercury link is not broken by cold dilute hydrochloric acid. They do not give mercuric sulphide readily on treatment with hydrogen sulphide. Potassium iodide solution decomposes them with the quantitative liberation of alkali hydroxide.

The bishydroxymercuric-compounds are converted into sulphatomercuri-derivatives (I) by 10% sulphuric acid, and their solutions in dilute aqueous sodium hydroxide give chloromercuri-derivatives (II) and mercaptomercuri-compounds (III) when treated with dilute hydrochloric acid and with carbon disulphide, respectively.



(I)



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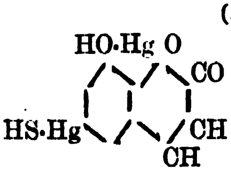

(III)

Mercuric acetate was made to react with solutions of the coumarins mentioned above in 5% aqueous sodium hydroxide. Its action on coumarin-6-sulphonic acid was also examined. The course of the reaction with coumarin is similar to that depicted above, the final product containing HgOAc in positions 6 and 8.

On treatment with dilute hydrochloric acid and with hydrogen sulphide the bisacetoxy-mercuricoumarins give results similar to those obtained with the bishydroxymercuri-coumarins. Treatment with potassium iodide solution, however, liberates only two equivalents of alkali instead of four :

$$C_9H_4O_2(Hg.OAc)_2 + 8KI + 2H_2O \xrightarrow{\text{cold}} C_9H_5O_2(HgOAc) + K_2HgI_4 + CH_3.CO_2K + 4KI + KOH + H_2O \xrightarrow{\text{heated}} C_9H_6O_2 + 2K_2HgI_4 + 2CH_3.CO_2K + 2KOH.$$

6 : 8-*Bisacetoxymercuricoumarin*, when treated with sodium thiosulphate solution, is converted into a compound, $C_9H_4O_2 <^{Hg}_{Hg}> C_9H_4O_2$ (IV), which readily gives a sulphato-mercuri-derivative (compare Dimroth, *Ber.*, 1902, **35**, 2853; Maynard, *J. Amer. Chem. Soc.*, 1924, **46**, 1510; Pesci, *Gazzetta*, 1899, **29**, 394).

The effect of substituents on the mercuration of coumarins by mercuric acetate is, in general, similar to that in the case of mercury acetamide. The main differences are; (1) 6-nitro-coumarin yields 6 : 8-bisacetoxymercuricoumarin; so also does coumarin-6-sulphonic acid; (2) 3-acetyl-4-methyl-coumarin gives a bisacetoxymercuri-derivative; (3) 4-phenyl-3-allyl (or benzyl) coumarin yields a hydroxymercuri-acetoxymercuri-derivative. Compounds of the last type, when treated with potassium iodide solution, liberate only three equivalents of potassium hydroxide. 6-Acetoxy-mercuri-4 : 7-dimethylcoumarin, similarly treated, liberates one equivalent of alkali.

The constitutions assigned to the mercury compounds now described are based on the following considerations :

(1) The mercury-containing substituent has not opened the ethylenic link, because (*a*) the behaviour of the compounds towards sodium carbonate and bicarbonate is like that of coumarin itself, (*b*) cinnamic acid, which contains a double bond in a similar position, is not mercurated when similarly

treated (Billmann, *Ber.*, 1902, **35**, 2576; 1910, **43**, 574), and (c), the compounds decolorise potassium permanganate soultion as do the coumarins.

(2) The mercury atom has entered the nucleus, because (a) all attempts to mercurate coumarin directly failed, but when the hydroxyl group was generated by means of 5% sodium hydroxide solution, the phenolic compound was mercurated at once. A phenolic hydroxyl group not only facilitates mercuration, but also appears to exert an oreenting influence (Mameli, *Gazzetta*, 1922, **52**, i, 352; ii, 18, 23, 113; 1926, **56**, 948), mercuration taking place in the *p*- or *o*-positions to it; these become positions 6 and 8 when the coumarin ring is formed, That the mercury is in positions 6 and 8 is further proved by the facts that coumarins with a substituent in position 5 or 7 give dimercurated compounds, whereas those with a substituent in position 6 or 8 give only mono-mercurated derivatives. (*b*) From a study of known mercury compounds, such a those of *allo*cinnamic acid, it appears that the mercury atom in the nucleus is not removed by dilute hydrochloric acid or hydrogen sulphide (Whitmore, " Monograph on Mercury Compounds "). (*c*) The reaction of the compounds with potassium iodide solution is of the same type as that of the mercurated phenols (Whitmore, *op. cit.*). (*d*) Iodination of dimercurated coumarin gave a *tri-iododihydrocoumarin*, which on oxidation furnished 3 : 5-di-iodosalicylic acid.

From the following facts, it appears that the mercury-containing substituent in position 6 is more reactive than that in position 8 : (*a*) the reaction of a bishydroxymercuricoumarin with potassium iodide solution liberates two equivalents of potassium hydroxide in the cold and two more on heating; (*b*) in the reactions with carbon disulphide, dilute hydrochloric acid, and 10% sulphuric acid, only one of the two substituents is attacked; (*c*) 6-nitrocoumarin on mercuration is converted into 6-hydroxymercuricoumarin.

EXPERIMENTAL.

The coumarins required for the work were prepared mostly by the condensation of phenols with β-ketonic esters in presence of sulphuric acid; a few were obtained by the condensation of salicylaldehyde with β-ketonic esters in presence of piperidine. For the preparation of 7-hydroxy-3-allyl- and -3-benzyl-coumarin phosphorus oxychloride was used as condensing agent, with excellent results (Naik and Trivedi, J. *Indian Chem. Soc.*, 1929, **6**, 801).

6 : 8-B*ishydroxymercuricoumarin.*—Coumarin (2 g.) was dissolved in 5% sodium hydroxide solution (100 c. c.), and the excess of alkali neutralised with dilute acetic acid. The yellow precipitate obtained on addition of a solution of mercury acetamide (Scholler and Schrauth, *Ber.*, 1909, **42**, 784) (10 g.) in water was washed with water, alcohol, and ether (Table I, No. 1).

6 : 8-B*ishydroxymercuricoumarin* is insoluble in most organic solvents, but dissolves in dilute aqueous sodium hydroxide. A suspension (0·3365 g.) in water (50 c. c.) was treated with a solution of potassium iodide (3 g.) and the liberated alkali titrated (phenolphthalein) against 0·0686*N*-hydrochloric acid; in the cold 1·90 equivs., and after heating a further 2·05 equivs., were neutralised. The total of 3·95 equivs. indicates that the rupture of the C–Hg link was complete.

The addition of dilute hydrochloric acid to a solution of the mercury compound in aqueous hydroxide gave a white bulky precipitate, consisting of the *chloromercuri*-compound (II), which was washed whith water and alcohol (Found : Cl, 6·3. $C_9H_5O_3Hg_2Cl$ requires Cl, 5·9%).

Heated for ½ hour in 10% sulphuric acid, the mercuration product gave a white precipitate, the *sulphatomercuri*-compound (I), which was washed with water and alcohol (Found; S, 2·9. $C_{18}H_{10}O_{10}Hg_4S$ requires S, 2·65%).

A few drops of carbon disulphide were added to an alkaline solution of the mercuration product, the mixture was shaken for a few minutes, and the excess of alkali neutralised with dilute acetic acid. The yellow precipitate obtained (Table III, No. 1) was washed with water, alcohol, and ether.

The mercuration product was heated with 0·1*N*-iodine for 15 minutes. The brown precipitate formed was crystallised from alcohol (Found : I, 71·9. $C_9H_8O_2I_3$ requires I, 72·4%) and oxidised with alkaline potassium permanganate; 3 : 5-di-iodosalicylic acid, m. p. 220—222°, was produced.

6-*Hydroxymercurithiocoumarin.*—Thiocoumarin (1 g.), dissolved in alcohol, was treated with an alcoholic solution of mercury acetamide (5 g.). The yellow product (Table I, No. 18) was washed with hot water, alcohol, and ether.

6:8-*Bisacetoxymercuricoumarin.*—Mercuration of coumarin with mercuric acetate was carried out in aqueous solution through the neutral sodium salt. The yellow precipitate (Table II, No. 1) was washed with alcohol and ether. It was insoluble in all organic solvents, but soluble in dilute sodium hydroxide solution.

Its suspension (0·516 g.) in water was treated with a solution of potassium iodide (2 g.) and the liberated alkali was titrated against 0·0492*N*-hydrochloric acid; in the cold 15·5 c.c., and hot, a further 17·5 c.c., of the acid were required. In all, 2·03 equivs. of the alkali were liberated, indicating the complete rupture of the C—Hg link.

The bisacetoxymercuri-compound (1 g.), suspended in a solution of sodium thiosulphate, was heated for ½ hour, and kept for 8 days. The black precipitate which had formed was removed, and the filtrate boiled for 2 hours. The red precipitate IV) thus produced was collected, washed with

TABLE I.

Reaction Products of Coumarins and Mercury Acetamide.

No.	Coumarin derivative produced.	Formula.	Colour.	Temp. of colour change.	% Hg found.	% Hg calc.
1	6 : 8-Bishydroxymercuri-	$C_9H_6O_4Hg_2$	Yellow	225°	69·6	69·2
2	7-Hydroxy-6 : 8-bishydroxymercuri-4-methyl-	$C_{10}H_8O_5Hg_2$	Orange	270	65·3	65·7
3	7-Amino-6 : 8-bishydroxymercuri-4-methyl-	$C_{10}H_9O_4NHg_2$	Deep red	253	65·4	65·8
4	6-Hydroxymercuri-4 : 7-dimethyl-	$C_{11}H_{10}O_3Hg$	Light yellow	261	52·0	51·3
5	5-Hydroxy-6-oxyhydroxymercuri-8-hydroxymercuri-4-methyl-	$C_{10}H_8O_6Hg_2$	Deep yellow	160	64·2	64·1
6	Oxyhydroxymercuri-4-methyl-	$C_{10}H_8O_4Hg$	Brown	218	50·4	51·0
7	6-Hydroxymercuri-	$C_9H_6O_3Hg$	Yellowish-brown	218	55·4	55·2
8	8-Hydroxymercuri-4 : 6-dimethyl-	$C_{11}H_{10}O_3Hg$	Light yellow	198	51·1	51·3
9	6-Hydroxymercuri-4 : 8-dimethyl-	$C_{11}H_{10}O_3Hg$	Yellowish-brown	243	50·9	51·3
10	7-Hydroxy-6 : 8-bishydroxymercuri-4 : 5-dimethyl-	$C_{11}H_{10}O_5Hg_2$	Buff	—	64·8	64·4
11	7-Hydroxy-6 : 8-bishydroxymercuri-4-methyl-3-allyl-	$C_{13}H_{12}O_5Hg_2$	Deep orange-red	—	62·2	61·8
12	7-Hydroxy-6 : 8-bishydroxymercuri-3-benzyl-4-methyl-	$C_{17}H_{14}O_5Hg_2$	Deep red	272	56·8	57·2
13	7-Hydroxy-6 : 8-bishydroxymercuri-4-phenyl-	$C_{15}H_{10}O_5Hg_2$	Deep red	260	59·3	59·7
14	6 : 8-Bishydroxymercuri-3-carboxy-	$C_{10}H_6O_6Hg_2$	Lemon-yellow	251	65·0	64·3

15	6 : 8-Bishydroxymercuri-3-acetyle-	$C_{10}H_8O_5Hg_2$	Yellow	—	64·1	64·5
16	6-Hydroxymercuri-3-benzoyl-	$C_{16}H_{10}O_4Hg$	Deep yellow	230	42·8	42·4
17	6 : 6′-Bishydroxymercuriketodi-	$C_{19}H_{10}O_7Hg_2$	Yellow	235	52·6	53·3
18	6-Hydroxymercuri-thio-	$C_9H_6O_2SHg$	Yellow	—	52·7	52·9
19	Hydroxymercuri-6-methyl-1 : 2-α-naphthapyrone	$C_{14}H_{10}O_3Hg$	Light red	161	47·6	47·0
20	Hydroxymercuri-6-methyl-3 : 4-β-naphthapyrone	$C_{14}H_{10}O_3Hg$	Light yellow	188—198	47·4	47·0

TABLE II.

Reaction Products of Coumarins and Mercuric Acetate.

No.	Coumarin derivative produced.	Formula.	Colour.	Decomposition.	% Hg found.	% Hg calc.
1	6 : 8-Bisacetoxymercuri-	$C_{13}H_{10}O_6Hg_2$	Yellow	248°	60·85	60·5
2	7-Hydroxy-6 : 8 bisacetoxymercuri-4-methyl-	$C_{14}H_{12}O_7Hg_2$	Deep yellow	208	58·5	57·9
3	7-Amino-6 : 8-bisacetoxymercuri-4-methyl-	$C_{14}H_{13}O_6NHg_2$	Deep red	270	58·45	57·9
4	6-Acetoxymercuri-4 : 7-dimethyl-	$C_{13}H_{12}O_4Hg$	Faint pink	—	46·1	46·3
5	5-Hydroxy-6-oxyacetoxymercuri-8-acetoxymercuri-4-methyl	$C_{14}H_{12}O_8Hg_2$	Deep yellow	145	56·9	56·5
6	6 : 8-Bisacetoxymercuri-	$C_{13}H_{10}O_6Hg_2$	Yellow	—	59·85	60·5
7	6-Oxyacetoxymercuri-4-methyl-	$C_{12}H_{10}O_5Hg$	Brown	230	45·6	46·1

TABLE II.—*Reaction Products of Coumarins and Mercuric Acetate*—(Concld.).

No.	Coumarin derivative produced.	Formula.	Colour.	Decom-position.	% Hg found.	% Hg calc.
8	8-Acetoxymercuri-4 : 6-dimethyl	$C_{13}H_{12}O_4Hg$	Yellowish	238	46·7	46·3
9	6-Acetoxymercuri-4 : 8-dimetyl-	$C_{13}H_{12}O_4Hg$	—	—	46·6	46·3
10	7-Hydroxy-6 : 8-bisacetoxymercuri-4 : 5-dimethyl-	$C_{15}H_{14}O_7Hg_2$	Yellow	210	56·9	56·6
11	7-Hydroxy-6-hydroxymercuri-8-acetoxymercuri-4-methyl-3-allyl-	$C_{15}H_{14}O_6Hg_2$	Orange-yellow	212	58·4	57·9
12	7-Hydroxy-6-hydroxymercuri-8-acetoxymercuri-3-benzyl-4-methyl-	$C_{19}H_{16}O_6Hg_2$	Deep red	—	54·6	54·05
13	7-Hydroxy-6-hydroxymercuri-8-acetoxymercuri-4-phenyl-	$C_{17}H_{12}O_6Hg_2$	Deep red	—	55·8	56·2
14	6 : 8-Bisacetoxymercuri-3-carboxy-	$C_{14}H_{10}O_8Hg_2$	Yellow	260	57·0	56·65
15	6 : 8-Bisacetoxymercuri-3-acetyl-	$C_{15}H_{12}O_7Hg_2$	Yellow	215	57·4	56·8
16	6-Acetoxymercuri-3-benzoyl-	$C_{18}H_{12}O_5Hg$	Deep yellow	190	39·2	39·3
17	6 : 6'-Bisacetoxymercuriketodi-	$C_{23}H_{14}O_9Hg_2$	Yellow	192	47·5	47·9
18	6-Acetoxymercuri-thio-	$C_{11}H_8O_3SHg$	Pink	252	47·9	47·6
19	Acetoxymercuri-6-methyl-1 : 2-α-naphthapyrone	$C_{16}H_{12}O_4Hg$	Light red	220	42·1	42·7
20	Acetoxymercuri-6-methyl-3 : 4-β-naphthapyrone	$C_{16}H_{12}O_4Hg$	Light yellow	196	42·3	42·7
21	6 : 8-Bisacetoxymercuri- (from coumarin-6-sulphonic acid)	$C_{13}H_{10}O_6Hg_2$	Yellow	—	61·0	60·5

TABLE III.

Reaction Products of Mercurated Coumarins (Table I) and Carbon Disulphide.

No.	Coumarin derivative produced.	Formula.	Colour.	Decomposition.	% S found.	% S calc.
1	6-Mercaptomercuri-8-hydroxymercuri-	$C_9H_6O_3SHg_2$	Yellow	182°	5·3	5·4
2	7-Hydroxy-6-mercaptomercuri-8-hydroxymercuri-4-methyl-	$C_{10}H_8O_4SHg_2$	Deep red	187	4·85	5·10
16	6-Mercaptomercuri-3-benzoyl-	$C_{16}H_{10}O_3SHg$	Red	—	6·9	6·6
17	6 : 6'-Bismercaptomercuriketodi-	$C_{19}H_{10}O_5S_2Hg_2$	—	—	8·5	8·2
19	Mercaptomercuri-6-methyl-1 : 2-∝-naphthapyrone	$C_{14}H_{10}O_2SHg$	—	—	7·7	7·3

alcohol, and dried. It became black at about 195° (Found : Hg, 58·5. $C_{18}H_8O_4Hg_2$ requires Hg, 58·1%).

Action of Iodine on 7-Hydroxy-6 : 8-bisacetoxymercuri-4-methylcoumarin.—The compound (1 g.), suspended in water (50 c.c.), was treated slowly with a solution of iodine and heated until no further absorption was observed. The product, crystallised from alcohol, melted at 172° (Found : I, 68·6. $C_{10}H_7O_3I_3$ requires I, 68·5%).

6-*Acetoxymercurithiocoumarin.*—When alcoholic solutions of thiocoumarin (1 g.) and mercuric acetate (5 g.) were mixed, a pinkish precipitate (Table II, No. 18) separated; it was washed with alcohol and ether.

The authors express their gratitude to the Government of His Highness the Maharaja Gaekwar of Baroda for a grant.

The College, Baroda (India).

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XXXIII.—Investigations on Hyponitrites. Part I. Sodium Hyponitrite : Preparation and Properties.

By James Riddick Partington and
Chandulal Chhotalal Shah.

Sodium hyponitrite required for the present work was prepared by a modification of the method of Divers (J., 1899, **47**, 97). Three other methods (Joanis, *Compt. rend.*, 1894, **118**, 718; Weitz and Vollmer, *Ber.*, 1924, **57**, *B.* 1015; Scott, *J. Amer. Chem. Soc.*, 1927, **49**, 986) were tried and found to give hyponitrite, but the method adopted here was found to be the most suitable, as regards both cost and purity of the product. We were not able to obtain it in the pure white form by the method of Weitz and Vollmer.

Three solid hydrates of the salt have been reported, the penta- (Divers, *loc. cit.*), the hexa- (Menke, J., 1878, **33**, 401), and the ennea-hydrate (Weitz and Voller, *loc. cit.*). We find that the solid salt exists in the form of two different hydrates. From a concentrated solution of sodium hydroxide, it separates on standing in a vacuum over sulphuric acid in the form of small granules of the pentahydrate. If this or the anhydrous salt is redissolved in water, and the solution concentrated over sulphuric acid in a vacuum, or the solid precipitated by a large excess of alcohol, the *octahydrate* is formed. In the first case, the octahydrate forms short thick needles, and in the second it appears as very small crystals. The hexa- and the ennea-hydrate could not be obtained, and very probably these have been mistaken for the above two hydrates. Divers could not obtain the salt in the crystalline form, and denied the statement made by Jackson (P., 1893, **12**, 210), who obtained it in needles.

Analysis.—The salt, in either the anhydrous or the hydrated state, has not been analysed previously, except one analysis each by Divers, Menke, and Weitz and Vollmer

(*loc. cit.*). Menke estimated the nitrogen in the substance by heating it with soda-lime and determining the amount of ammonia formed. We found no trace of ammonia either under these conditions or when the salt was treated with Devarda's alloy and potassium hydroxide. Nitrogen in hyponitrites, in general, however, can be estimated by a modification of Dumas's method. The dry salt is mixed with fused sodium hydrogen sulphate and heated in a combustion tube, the gases evolved being passed over hot reduced copper gauze, and the liberated nitrogen measured. Kirschner (*Z. anorg. Chem*, 1898, **16**, 424) used copper powder instead of sodium bisulphate. This method gives good results with other salts, but fails in the case of the sodium compound, the results of the nitrogen analysis being always too low, apparently because some nitrogen as sodium nitrate remains undecomposed by sodium hydrogen sulphate, even at a red heat. The residue was, in fact, found to contain sodium nitrate. Since no suitable method could be found for the determination of nitrogen in the sodium salt, the hyponitrite radical was determined as the silver salt; but as silver carbonate and nitrite are also insoluble in a neutral solution, the sodium salt was examined for the presence of both of these. The amount of nitrite in the salt was found to be less than 0·001%, and no carbonate was detected.

Action of Hydriodic Acid.—Various views are held as to the action of hydriodic acid on hyponitrites. A solution of the sodium salt does not immediately give any blue colour with hydriodic acid and starch, although this colour develops in 2—3 minutes. We believe that this result is due to small traces of nitrous acid present in the preparation. A solution which has been kept for 24 hours behaves similarly, showing that the amount of nitrous acid does not appreciably increase, though a sensitive colorimetric determination with Griess reagent shows that nitrous acid does increase somewhat in such a solution. In a freshly prepared solution, the content of sodium nitrite was found to be $4{\cdot}2 \times 10^{-4}$ %, and in the

same solution after 24 hours it was $6{\cdot}3 \times 10^{-4}\%$, which increased to $7{\cdot}3 \times 10^{-4}\%$ at the end of one week. Probably in solution the salt decomposes according to the equation

$$3Na_2N_2O_2 + 2H_2O = 2NaNO_2 + 4NaOH + 2N_2 \quad . \quad (1)$$

but the amount of nitrous acid formed is too small for macro-estimation. The solution does not give the diphenylamine test.

Thermal Decomposition of the Solid.—The action of heat on the solid anhydrous salt has been studied by Divers (*loc. cit.*), who states that it is stable up to 300°, but at higher temperatures decomposes as follows

$$3Na_2N_2O_2 = 2NaNO_2 + 2Na_2O + 2N_2 \qquad (2)$$

Ray and Ganguli (J., 1907, **91**, 1399) find that the products of the action of heat on the silver salt consist of silver, silver nitrate, nitrogen, and nitric oxide; and on the mercury salt, of mercury, mercuric oxide, nitric and nitrous oxides, together with some nitrogen and mercurous nitrate. In contrast to these two salts, we find that the sodium salt decomposes according to the equation given by Divers [(2) above] when heated in a vacuum, the decomposition occurring suddenly and explosively at 260—265°, leaving a red residue which becomes yellow on cooling. The solid on analysis was found to consist of equimolecular proportions of sodium nitrite and sodium oxide, while the gas evolved was pure nitrogen.

When the dry salt is heated with sodium hydrogen sulphate, the gaseous products consist of nitrous and nitric oxides and nitrogen, while, as stated above, even at a red heat some sodium nitrate remains in the solid residue. Probably the decomposition proceeds simultaneously according to the equations

$$Na_2N_2O_2 + 2NaHSO_4 = 2Na_2SO_4 + H_2O + N_2O \quad . \qquad (3)$$

$$3Na_2N_2O_2 + 4NaHSO_4 + 2NaNO_2 + 4Na_2SO_4 + 2H_2O + 2N_2 \qquad (4)$$

$$2Na_2N_2O_2 + 4NaHSO_4 = 4Na_2SO_4 + N_2 + 2H_2O + 2NO \quad . \qquad (5)$$

$$3NaNO_2 + 2NaHSO_4 = 2Na_2SO_4 + NaNO_3 + H_2O + 2NO \qquad (6)$$

Aqueous solutions of the salt instantaneously decompose in a vacuum to the extent of 50%, giving nitrous and nitric oxides and nitrogen, the main product being nitrous oxide (68·5%). The action may be represented by equations (3) and (5), H_2O being substituted for $NaHSO_4$. If the pressure is not below 40 mm., the solution does not decompose abruptly, but does so slowly, the decomposition mainly proceeding according to equation (3). No nitrate or nitrite can be detected in the solution.

Action of Acids.—Ray and Ganguli (J., 1907, **91**, 1866) studied the action of dilute mineral acids on the silver and the mercurous salt, and showed that the former is completely docomposed by these acids, whilst the latter is only partly decomposed, except by hydrochloric acid. We have examined the action of dilute sulphuric and hydrochloric acids on the sodium salt, and find that the reaction is the same as in aqueous solution; the percentage decomposition is a little higher and the proportion of nitrogen and nitric oxide is slightly greater, thus showing that the reaction (5) is favoured by acids. No nitrate or nitrite appears to be formed during the reaction.

The salt is completely decomposed by concentrated sulphuric acid. Nitric acid and traces of nitrous acid are formed besides nitrous and nitric oxides and nitrogen. The reaction is very vigorous and the whole vessel becomes filled with white fumes, the solid salt being so much heated at places that it glows. The main reaction (65%) is represented by equation (3). All the reactions (3), (4), (5) and (6) probably occur, and also probably, in addition :

$$5Na_2N_2O_2+8H_2SO_4=2NaNO_3+8NaHSO_4+4H_2O+4N_2 \quad (7)$$

Oxidation with Potassium Permanganate.—Various workers have examined the oxidation of hyponitrous acid and of sodium and other hyponitrites in presence of sulphuric acid by means of permanganate, but have reached very different conclusions. Hantzsch and Sauer (*Annalen*, 1897, **299**, 67)

prepared a solution of the free acid by shaking $N/100$-hydrochloric acid with a weighed amount (excess) of silver hyponitrite; the amount of potassium permanganate used by such a solution was less than that required by the equation

$$H_2N_2O_2 + 4O = 2HNO_3 \qquad (8)$$

Similarly, Kirschner (*loc. cit.*,) treated weighed amounts of the barium, calcium, strontium, and silver salts with acid potassium permanganate and also obtained low values. On the contrary, Divers (*loc. cit.*), using $N/20$-solution of the acid, and Thum (*Monatsh.*, 1893, **14**, 294), using $N/100$-solution of the acid, in both cases prepared from silver hyponitrite and hydrochloric acid, obtained values showing that the oxidation proceeds to completion according to equation (8) Recently, Raschig (" Schwefel- und Stickstoffstudien," 1924) has shown that the action of acidified potassium permanganate proceeds according to the equation

$$H_2N_2O_2 + 2O = 2HNO_2 \qquad (9)$$

and differs from the action of subsequently acidified potassium permanganate (acid added 15 minutes after the permanganate solution), which proceeds according to equation (8) above. As is well known, nitrous acid is oxidised quantitatively to nitric acid by potassium permanganate in presence of acids. To avoid this difficulty, Rasching supposes that an anhydride, N_2O_3, different in constitution from the anhydride of nitrous acid and stable towards permanganate in acid solution, is formed. In his experiments he used a solution of the sodium salt obtained by shaking silver hyponitrite with staturated sodium chloride solution.

We have repeated these experiments, using solutions of different concentrations and prepared in different ways, and we think that a portion of the hyponitrous acid is always oxidised to nitric acid according to equation (8), the other portion decomposing into nitrous oxide and water according to equation (3). Owing to the spontaneous decomposition of

solutions of hyponitrites and hyponitrous acid, the results obtained are invariably low as can be seen from Table II. Another cause for the low values is the fact that silver hyponitrite is not completely decomposed by shaking with hydrochloric acid (Ray, De, and Dhar, J., 1913, **103**, 1562), or with sodium chloride (Divers, *loc. cit.*).

Since aqueous solutions of the salt decompose in a vacuum, as shown above, they were not used for examining the products of oxidation formed in a vacuum. The results obtained with the solid sodium salt show that the above conclusion regarding the action of permanganate on hyponitrous acid *viz.*, that a portion of it is oxidised to nitric acid and the other portion decomposes into nitrous oxide, is correct. In the presence of acidified potassium permanganate, 65% of the salt decomposes, giving nitrous oxide and nitrogen. The remaining 35% is oxidised to nitric acid. But if the acid is added 15 minutes after the potassium permanganate solution, 48% of the salt decomposes into nitrous oxide and nitrogen, and the rest is oxidised to nitric acid. The formation of nitrogen probably occurs according to equation (5), the nitric oxide simultaneously formed being oxidised to nitric acid. Thus the low values obtained by Rasching are to be attributed rather to the greater decomposition suffered by hyponitrous acid than to the formation of a hypothetical oxide, N_2O_3. In his attempt to separate this N_2O_3, he failed to account for one-third of the total nitrogen, which very probably escaped before he began his estimation.

Reduction.—Among the products of reduction of hyponitrous acid, four substances, *viz.*, nitrogen, hydroxylamine, hydrazine, and ammonia, are likely to be formed. By reduction with zinc and acetic acid, Devarda's alloy and potassium hydroxide, aluminium amalgam, sodium bisulphite, stannous chloride, titanous chloride, and sodium hydrosulphite (hyposulphite), we find that none of the last three is formed, though von Brackel (*Ber.*, 1900, **33**, 2115) claims to have obtained

hydrazine by reduction with zinc and acetic acid and also with sodium bisulphite. In the case of sodium hydrosulphite (alkaline), no nitrogen either appears to be formed. Coblens and Bernstein (*J. Physical Chem.*, 1925, **29**, 750) claim to have reduced silver hyponitrite to ammonia by the successive action of stannous chloride and titanous chloride. We were unable to obtain any ammonia by the action of these reagents on sodium hyponitrite solution. Traces of ammonia sufficient for colorimetric estimation by Nessler reagent were found in the solution, but this is probably due to impurities rather than to the reduction of the hyponitrite.

Table I summarises the foregoing results in the form of a nitrogen balance.

Experimental.

Preparation of Sodium Hyponitrite.—25 G. of pure sodium nitrite (Divers, J., 1899, **47**, 85) are dissolved in 50 c.c. of water. Sodium amalgam, prepared by dissolving 25 g. of sodium in 140 c.c. of mercury, is slowly added to the above solution contained in a round-bottomed flask. During the addition the solution is kept cold by running water. After all the amalgam is added, the flask is vigorously shaken and cooled till no more heat develops. The whole is then transferred to a thick-walled separating funnel, the solid adhering to the flask being twice washed with very small amounts of water, and shaken continuously for one hour to reduce any nitrite which might have been precipitated along with the hyponitrite from the strongly alkaline solution. The amalgam is then separated. The sodium hyponitrite is filtered off through asbestos, without unduly exposing the liquid to the action of air, which can best be done by passing a current of carbon dioxide-free air or nitrogen over the solution being filtered. The solid is then taken out and repeatedly triturated with alcohol till the pulp-like mass falls to a fine powder, which is then filtered and washed with the same reagent. It

is redissolved in the least amount of water, and filtered from suspended impurities. The solution is then concentrated over sulphuric acid in a vacuum. The vessel should preferably be covered, as considerable bumping occurs. On the third or fourth day thick short needles separate. These are crushed and triturated with alcohol, filtered, and washed with alcohol and ether. The salt so prepared is the *octahydrate* (Found : Na, 18.05; N_2O_2, 24.7; H_2O, 55.5. $Na_2N_2O_2,8H_2O$ requires Na, 18.4; N_2O_2, 24.0; H_2O, 57.6%). When left for 24 hours over concentrated sulphuric acid in a vacuum, it becomes anhydrous (Found : Na, 42.3; N_2O_2, 54.1. Calc. for $Na_2N_2O_2$: Na, 43.4; N_2O_2, 56.6%). The yield of the anhydrous salt is 19%. Its specific gravity is 1.726 at 25°.

For preparing the pentahydrate, sodium nitrite is dissolved in 75 c. c. of water. After separation of the amalgam, the solution is filtered through asbestos, and the filtrate left in a vacuum over sulphuric acid. After about 25 days, small granules separate. These are filtered in a small Gooch crucible without asbestos and washed with alcohol, They are then taken out, triturated with alcohol, filtered, and washed with alcohol and ether (Found : Na, 23.9; N_2O_2, 29.8; H_2O, 45.1. Calc. for $Na_2N_2O_2,5H_2O$: Na, 23.5; N_2O_2, 30.6; H_2O, 45.9%).

In studying the action of various reagents in a vacuum, the apparatus shown in Fig. 1 (for fiig. see J. C. S. 1931, p. 2077) was used. The substance was weighed out in the small tube A and carefully introduced into the flask. The solution, the action of which it was desired to study, was contained in the side tube B or D. In cases where it was necessary to study the action of two reagents in succession, these were separately introduced into B and D. The vessel was then attached to the Sprengel pump and evacuated, and the solutions added to the substance through the three-way tap E. A small amount of air remains in the tap (calculated, 1.1 c.c.) and in the analysis this volume is deducted from the amount of nitrogen.

For studying the action of heat, the substance was weighed in the tube shown in Fig. 2. (See for fig. J. C. S. 1931 p. 2077 The spiral at the top, which contains some glass wool. prevents escape of solid when it suddenly decomposes. This tube is heated in a Pyrex tube, having a ground-in glass thermometer and attached to the pump.

Action of Heat.—(i) 0·1009 G. of the hyponitrite gave 13·9 c.c. of nitrogen (at S.T.P.). The residue weighed 0·0826 g. and required 13·9 c.c. of 0·0935*N*-hydrochloric acid for neutralisation (phenolphthalein) and 11·2 c.c. of 0-11*N*-potassium permanganate solution. (ii) 0·1236 G. left a residue weighing 0·0994 g. and required 17·0 c.c. and 14·4 c.c. of the above reagents respectively.

The hyponitrite remains unchanged to 260°. At 260—265°, it begins to melt, effervesces, and suddenly decomposes, turning first yellow and then red. After cooling, the residue is yellow.

Action of Sodium Hydrogen Sulphate.—The hyponitrite was weighed in a porcelain boat, mixed with 1 g. of sodium hydrogen sulphate, and introduced into a short length of combustion tubing, which was then evacuated. (i) 0·1730 G. gave 7·6 c.c. of nitrous oxide, 3·6 c.c. of nitric oxide, and 16·1 c.c. of nitrogen. The residue contained nitrate (diphenylamine test) and traces of nitrite (potassium iodide and starch). (ii) 0·1297 G. gave respectively 9·8, 2·2, and 13·2 c.c. of these three gases. The residue gave 4·0 c.c. of nitric oxide (estimation of nitric acid by Crum-Frankland method).

In this experiment, and in the action of concentrated sulphuric acid, a washing tube containing potassium hydroxide was interposed between the pump and the apparatus, but no nitrate or nitrite was detected in it (diphenylamine test).

Action of Water.—(i) 0·1038 G. of hyponitrite gave with 20 c.c. of water 7·9 c.c. of nitrous oxide, 2·5 c.c, of nitrogen, and 1·0 c.c, of nitric oxide; on the next day 2·3 c.c. more of

the first gas were evolved. (ii) 0·1142 G. gave with 10 c.c. of water 8·1, 2·7, and 1·1 c.c. of these gases respectively. The solution did not give any test for nitrate or nitrite, but showed the presence of undecomposed hyponitrite by giving a yellow precipitate with silver nitrate.

Action of Acids.—This is shown in the following table. With the dilute acids the resulting solution gave the same reactions as with water, but with concentrated sulphuric acid, it contained nitrate and nitrite (the latter too small for estimation) and gave 1·6 c.c. of nitric oxide from the first solution.

Acid.	$Na_2N_2O_2$, g.	N_2O, c.c,	N_2, c.c.	NO, c.c.
H_2SO_4 (app. 3*N*), 20 c.c....	0·1557	15·5	4·8	7·4
	0·1040	11·2	3·2	4·0
HCl (app. 3*N*), 20 c,c. ...	0·1060	11·5	3·5	4·2
	0·1270	14·0	3·8	3·5
H_2SO_4 (*d* 1·84), 20 c.c....	0·1032	14·3	5·6	1·3
	0·1042	14·5	6·2	1·7

Action of Acidified Potassium Permanganate.—The solution used contained 0·5 g. of permanganate in 20 c.c, of 2*N*-sulphuric acid. The results of a second experiment are in parentheses. 0·1000 (0·1249) G. gave 12·3 (16·4) c.c. of nitrous oxide and 2·2 (2·5) c.c. of nitrogen. The solution was concentrated, and decolorised with oxalic acid, the excess of the latter being removed by slowly adding permanganate solution till a slight pink colour remained. An aliquot portion was taken for estimating nitric acid. The whole gave 14·0 (20·7) c.c. of nitric oxide.

Action of Potassium Permanganate followed by Sulphuric Acid.—The acid (20 c.c. of 2*N*) was added after the gases evolved during the addition of the permanganate (0·5 g. in 20 c.c. of water) had been collected (about 30 mins.) : 0·1054 g. gave before addition of acid 2·1 c c. of nitrous oxide and 2·1 c.c. of nitrogen; and after addition of acid 5·1 and 1·2 c.c. respectively.

The solution gave 23·3 c.c. of nitric oxide.

In examining the products of reduction, the presence of ammonia was tested with Nessler reagent, hydrazine by reduction of Fehling's solution and benzalazin test, and hydroxylamine by the benzoyl chloride-ferric chloride test.

Summary.

It has been shown that sodium hyponitrite occurs in the form of two hydrates—the penta- and the octa-hydrate. The action of heat and various reagents on the solid salt in a vacuum has been studied. The anhydrous salt, when heated, decomposes into sodium oxide, sodium nitrite, and nitrogen. It is partly decomposed by water, dilute sulphuric acid, and dilute hydrochloric acid, forming nitrous oxide, nitric oxide, and nitrogen; and completely by concentrated sulphuric acid, forming nitrous and nitric acids besides the above products.

TABLE I.

Percentages of the various products calculated in terms of nitrogen. (Theoretical total, 26·4%.)

Reaction :	N_2O.	N_2.	NO.	HNO_2.	HNO_3.	Total.
Heat	—	17·3	—	8·6	—	25·9
"	—	—	—	9·0	—	—
Water	9·5	3·0	0·6	—	—	13·1
"	8·9	3·0	0·6	—	—	12·5
H_2SO_4, dil ...	12·5	3·9	3·0	—	—	19·4
"	13·5	3·8	2·4	—	—	19·7
HCl, dil	13·6	4·1	2·5	—	—	20·2
"	13·8	3·7	1·7	—	—	19·2
H_2SO_4, conc. ...	17·3	6·8	0·79	—	0·8	25·69
"	17·4	7·4	1·0	—	—	25·8
$NaHSO_4$	5·5	11·6	1·3	—	—	18·4
"	9·4	12·7	1·1	—	1·9	25·1
$KMnO_4$, acidified.	15·4	2·8	—	—	8·8	27·0
" " ...	16·4	2·5	—	—	10·4	29·3
$KMnO_4$ then acid	8·9	3·9	—	—	13·8	26·2

TABLE II.

Source of solution.	Conc. of HNO, g. -mol. per litre.	Amount of $0{\cdot}1N$-$KMnO_4$ required by 10 c.c. of the sol. if its conc. was $0{\cdot}1N$: Acid at same time (I).	Acid after 15 mins. (II).	Ratio, (II)/(I).
Solid $Na_2N_2O_2$ dissolved in water	0·050	16·7	32·2	1·93
	0·050	14·2	27·4	1·93
Moist $Ag_2N_2O_2$ shaken with 0·1N-NaCl and diluted ...	0·025	—	9·0	—
BaN_2O_2 shaken with 0·1N-Na_2SO_4 and diluted ...	0·025	2·1	6·6	3·1
Moist $Ag_2N_2O_2$ shaken with 0·0935N-HCl and diluted...	0·0467	7·0	20·5	2·93
	0·0701	15·7	31·1	1·98
Moist $Ag_2N_2O_2$ shaken with satd. NaCl sol. and diluted	0·1335	14·6	29·3	2·07
	0·0482	11·1	23·8	2·16

By the action of potassium permanganate, a portion of the salt is oxidised to nitric acid and the other portion decomposes into nitrous oxide and sodium hydroxide, the proportions of the two depending on the experimental conditions, thus explaining the variable results obtained by different workers under slightly different conditions. The salt could not be reduced by stannous chloride, titanous chloride, sodium hydrosulphite, etc.

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East London College,
University of London.

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XXXVI.—Hyponitrites. Part II: Metallic Salts Part III: Esters.

By James R. Partington and Chandulal C. Shah.

Part II.

Calcium, strontium, and barium hyponitrites have been previoulу prepared in pure crystalline forms (Divers, J., 1899, **47**, 97; Maquenne, *Compt. rend*, 1889, **108**, 1303; Kirschner, Z. *anorg. Chem.*, 1898, **16**, 424), the first and last occurring as tetrahydrates, the second as a pentahydrate. We obtained all three in the cryst, form by pptn. on adding excess of a solution of the corresponding nitrate to $Na_2N_2O_2$ aq., washing with H_2O (at 40°), EtOH, and Et_2O, and drying on a porous plate (in the case of the Ca salt in a desiccator). The analyses of the products confirmed the formulæ stated.

We were unable to obtain the alleged basic lead hyponitrite, PbO,PbN_2O_2 (Kirschner, *loc. cit.*), or $Pb(OH)_2,PbN_2O_2$ (Neogi and Nandi, J., 1928, 1449), under any conditions, the normal salt, PbN_2O_2, prep, by Divers (*loc. cit.*), Kirschner (*loc. cit.*), and Thum (*Inaug. Diss.*, Prague, 1893; *Monatsh.*, 1893, **14**, 294), being always obtained in a pale yellow form by pptn. as in the case of alkaline-earth salts, and drying in a vac. If, instead of $Pb(NO_3)_2$, $Pb(OAc)_2$ is used, the ppt. is deep sulphur-yellow, and the salt detonates more violently when heated than that obtained from the nitrate. No attempt should be made to dry the Pb salt by heating. The other properties and the chemical composition of the two forms are the same.

A basic copper hyponitrite, $Cu_2(OH)_2N_2O_2$ (Divers; Thum; Kirschner; *locc. cit.*), could not be obtained. The ppt. formed on adding $CuSO_4$ aq. to $Na_2N_2O_2$ aq. was found (by Cu and N detmtn.) to have the composition CuN_2O_2.

Analyses—N was determined as described in Part I (J., 1931, 2071). The metal in Ca, Sr, Ba, and Pb hyponitrites was determined as sulphate, and in Cu hyponitrite

as oxide by maintaining the salt at a red heat for some time. Ca salt (Found : Ca, 23·21; N, 16·32. Calc. for $CaN_2O_2,4H_2O$: Ca, 23·29; N, 16·29%), Ba salt (Found : Ba, 51·37; N, 10·9. Calc. for $BaN_2O_2,4H_2O$: Ba, 50·97; N, 10·40%), Sr salt (Found : Sr, 36·9; N, 11·5. Calc. for $SrN_2O_2,5H_2O$: Sr, 36·86; N, 11·79%) Pb salts (Found, for yellow product : Pb, 77·32; N, 10·45. Found, for pale yellow product : Pb, 77·85; N, 10·3. Calc. for PbN_2O_2 : Pb, 77·57; N, 10·49%). Cu salt (Found : Cu, 50·97; N, 22·4. Calc. for CuN_2O_2 : Cu, 51·44; N, 22·67%).

Action of Air.—According to Kirschner, barium hyponitrite is decomp. by dry CO_2, while calcium hyponitrite is said by Divers to be very stable and a good hyponitrite to stock. Maquenne found that the alkaline-earth hyponitrites, do not completely lose H_2O of crystn. at 100°. Copper hyponitrite was found by Kirschner to be slightly hygroscopic. We found that these hyponitrites, when exposed to dry air or CO_2, remained practically unchanged in wt., whilst on exposure to air saturated with water vapour, there was a slight increase. The alkaline-earth hyponitrites retained their cryst. structure as seen under the microscope, even on exposure to ordinary air for several days, and the analysis of the salts exposed to air for a week did not show any change.

Scott (*J. Amer. Chem. Soc.*, 1927, **49**, 986) states that the Na salt prep. by him was non-hygroscopic, but this seems to have been based on appearance only. We exposed weighed amounts of the salt, prep. by our modification of Divers's method (J., 1931, 2075), to air, dry CO_2, and CO_2-free air saturated with water vapour. When exposed to air the salt at first rapidly absorbs moisture and increases in wt.; after about 3 days it begins to lose wt. When exposed to air saturated with water vapour in a desiccator, the increase in wt. continues for a considerable time, but the wt. immediately falls on exposure to the free air. The wt. of the dry salt remains unaffected on exposure over conc. H_2SO_4 in an atm.

of CO_2. A sample of sodium hyponitrite after exposure to air for a fortnight gave no characteristic yellow ppt. with $AgNO_3$. It appears that the dry salt is unaffected by CO_2 and is hygroscopic; in contact with water vapour or in solution it is slowly converted into the carbonate on exposure to ordinary air. The external appearance of the salt remains like that of anhyd. $MgSO_4$, even on absorption by the salt of twice its own wt. of H_2O.

Thermal Decomposition.—The thermal decomp. of the alkaline-earth salts has not been examined previously. Divers found that CuN_2O_2 gave H_2O, CuO, Cu_2O, N_2O, and NO.

The thermal decomp, of these salts cannot be represented by one equation, as in the case of $Na_2N_2O_2$, for although N_2O forms the major portion of the gaseous reaction products, it is always accompanied by NO and N. The alkaline-earth salts behave similarly and decompose at a temp. higher than 320°. The principal gaseous products are N_2O and N, with some NO. The solid residue is alk. and contains some nitrate and an amount of nitrite, which, although it can be detected qualitatively, is too small for determination. The following equations, in which R = Ca, Sr, or Ba, probably represent the decomposition :

$$RN_2O_2 = RO + N_2O \quad \ldots \quad \ldots \quad \ldots \quad (1)$$
$$5RN_2O_2 = R(NO_3)_2 + 4RO + 4N_2 \quad \ldots \quad (2)$$
$$2RN_2O_2 = 2RO + 2NO + N_2 \quad \ldots \quad \ldots \quad (3)$$

During the decomp. of lead and copper hyponitrites, N_2O is likewise the main product, but no nitrite or nitrate can be detected in the solid residue. The Pb salt is so explosive that the gaseous products could not be examined, but the greyish-yellow solid residue was PbO. Lead hyponitrite appears to be unstable even at 100°, at which temp. it slowly turns brown and loses wt., with evolution of N_2O. Since no nitrite or nitrate is found in the residue, it appears that the decomp., which is slow at lower temps. and occurs explosively at 150—160°, proceeds according to equation (1).

TABLE I.

Reagent.	Wt. of substance g.	N_2, c.c.	N_2O, c.c.	NO, c.c.	% of total N as N_2.	N_2O.	NO.	HNO_3
	$CaN_2O_2,4H_2O$.							
Heat	0·1088	2·8	9·2	1·7	20	65	6	9
"	0·1360	3·9	11·0	2·3	23	62	6	8
Dil. HCl ...	0·0954	0·9	4·0	1·7	7	32	7	0
Dil. H_2SO_4 ...	0·0994	—	1·3	—	0	10	0	0
Conc H_2SO_4 ...	0·1007	2·9	6·1	0·9	22	47	34	—
" ...	0·1235	3·2	7·9	1·0	20	49	31	—
Acid $KMnO_4$...	0·0970	0·2	4·2	—	2	33	0	65
$KMnO_4$+acid	0·1146	0·8	3·2	—	5	21	0	74
" ...	0·1082	0·8	3·0	—	6	21	0	73
	$BaN_2O_2,4H_2O$.							
Heat	0·1376	3·8	6·7	2·4	33	59	10	—
"	0·1032	3·0	5·1	1·9	35	59	8	—
Dil. HCl ...	0·1003	0·7	5·2	1·3	8	62	8	0
Conc. H_2SO_4 ...	0·1001	2·3	4·1	2·1	27	53	13	—
Acid $KMnO_4$ ...	0·1113	0·4	4·7	—	4	51	0	—
$KMnO_4$+acid ...	3·1042	0·7	3·2	—	8	37	0	—
	$SrN_2O_2,5H_2O$.							
Heat	0·1270	3·8	6·8	2·7	31	56	11	—
"	9·1010	3·0	5·4	2·1	31	57	11	—
$KMnO_4$+acid	0·1078	—	3·5	—	0	34	8	—
	PbN_2O_2.							
Dil. HNO_3 ...	0·1347	—	7·8	—	0	69	0	0
	CuN_2O_2.							
Heat	0·1042	1·1	16·8	2·0	6	89	5	0
"	0·0830	0·3	13·5	0·7	2	90	3	—
Dil. H_2SO_4 ...	0·1256	—	19·1	—	0	84	0	0
"	0·1137	—	17·4	—	0	84	0	0
Dil. HCl ...	0·0938	—	14·2	—	0	83	0	0
"	0·1029	—	15·4	—	0	83	0	0
Conc. H_2SO_4 ...	0·1020	4·2	10·8	3·5	23	58	10	—
" ...	0·0803	3·0	8·2	2·8	21	56	10	—
Acid $KMnO_4$ ...	0·1256	—	7·5	—	0	33	0	—

Unlike the Pb salt, copper hyponitrite is not explosive. It decomposes at 225—230°, and the gaseous products of decomp. are N_2O, NO, and N. The residue was shown by analysis to be CuO. Equations (1) and (3) represent the decomp.

Action of Water and Alkalis.—Water has no apparent action on the alkaline-earth, lead, or copper salts, and no gas is evolved when they are treated with water in a vac. $5N$-NaOH aq., when added to the salts, causes no evolution of gas, but hyponitrite can be detected in the solution. In the case of PbN_2O_2, which becomes perfectly white, the reaction is probably $PbN_2O_2+2NaOH = Pb(OH)_2+Na_2N_2O_2$. Even in this case the conversion is not complete, for the insol. residue contains some hyponitrite. For studying the action of heat and various reagents in a vac., the apparatus described in Part I (*loc. cit.*) was used. The results are given in Table I.

Action of Acids.—Our expts. on the reaction of dil. H_2SO_4 and HCl with $Na_2N_2O_2$ (*loc. cit.*) indicated that N_2O was the main product, and those now described are in general agreement with those of Cambi (*Gazzetta*, 1929, **59**, 770) on the action of $7N$-H_2SO_4 on PbN_2O_2 and 4N-acid on $Na_2N_2O_2$ in an atm. of CO_2, but not with his results in the case of the action of 7N-acid on CuN_2O_2. All the five hyponitrites behave towards acids like the Na salt; with the Ca, Sr, Ba, and Pb salts, the decomp. by H_2SO_4 is only slight, the Pb salt losing its colour very slowly. As in the case of the Na salt, no nitrate or nitrite is formed. Conc. H_2SO_4 completely decomposes all the salts at room temp., the products being similar.

Action of Oxidising Agents.—The action of $KMnO_4$ aq. on $H_2N_2O_2$ has been previously described (*loc. cit.*). Cambi (*loc. cit.*) has also studied the action of $KMnO_4$, I, and $K_3Fe(CN)_6$ on $Na_2N_2O_2$. and finds that nearly 60% of the hyponitrite N escapes as N_2O. He states that the amount of I absorbed depends on the p_H of the medium, and upon the order in which the reagents are added.

Potassium permanganate. Our results show that the nature of the acid has an influence on the amount of $KMnO_4$.

consumed, the results being always high with HOAc and HCl. In the titration with $KMnO_4$ a weighed amount of the salt was added to dilute acid, followed by excess of $KMnO_4$ aq. After 15 mins., standard $H_2C_2O_4$ was added and the excess determined by titration with $KMnO_4$.

Salt.	C.c. of 0·1N-$KMnO_4$ required for 1·0 g. of the salt.	Equivs. of $\frac{1}{2}$O required	Acid.
CuN_2O_2	267·8	3·3	H_2SO_4
	275·3	3·4	HNO_3
	338·4	4·2	HCl
$CaN_2O_2,4H_2O$	379·8	6·5	HCl
	267·8	4·6	HNO_3
	268·5	4·6	H_2SO_4
	269·5	4·6	HOAc+H_2SO_4
	344·2	5·9	AcOH
$BaN_2O_2,4H_2O$	270·7	7·3	H_2SO_4
	287·3	7·7	HNO_3
	292·4	7·9	HCl
	290·2	7·8	HOAc
$SrN_2O_2,5H_2O$	189·2	4·5	H_2SO_4
	198·6	4·9	HNO_3
	259·3	6·2	HCl
	259·5	6·2	HCl (excluding air.
	233·3	5·5	HOAc

PbN_2O_2 gave varying results. Some values obtained with HNO_3 are given, the figures in the last line corresponding with 1·0 g. of salt.

Wt., g.	0·0990	0·1129	0·1302	0·1336	0·1475	0·1645	0·1717	0·1773
Vol. required, c.c.	9·6	8·2	10·7	12·9	12·9	11·5	12·5	11·0
Vol. per g. ...	97·0	72·6	82·5	96·6	87·5	69·9	72·8	62·0

Iodine. The iodine titrations were carried out exactly in the manner described by Raschig ("Schwefel- und Stickstoffstudien," 1924, p. 103) (figures in parentheses give atoms of I per mol. of salt):

Amount of substance	0·1N-I absorbed, c. c.	0·1-I liberated by H_2SO_4, c.c.
10 c c 0·1335N-$Na_2N_2O_2$	4·0 (3·0)	3·5 (2·6)
0·1 g $CaN_2O_2,4H_2O$	10·8 (1·9)	5·9 (1·0)
0·1 g. $SrN_2O_2,5H_2O$	8·5 (2·0)	5·0 (1·2)
0·1 g. $BaN_2O_2,4H_2O$	9·6 (2·6)	5·1 (1·4)

The results were very discordant, and it is very doubtful whether the reactions proceed as represented by Raschig (*op. cit.*) *viz.*,

$$H_2N_2O_2 + I = HN_2O_2 + HI \qquad (1)$$
$$HN_2O_2 = HNO_2 + N \qquad (2)$$
$$HN_2O_2 = NO + NOH$$
$$2NOH = N_2O + H_2O \qquad (2a)$$
$$HNO_2 + HI = NO + I + H_2O \qquad (3)$$

(1) represents the absorption of I in HOAc solution, and (3) the liberation of I in presence of H_2SO_4. If the reaction proceeds smoothly according to (1), (2), and (3), all the I used in the first stage should be liberated in the third. Raschig found that only one-half is liberated, and hence suggested that (2) may occur in either of the two ways, the alternative being (2*a*).

Sodium hypochlorite. Oxidation by NaOCl gave the same results as that by $KMnO_4$. The action was investigated by adding excess of the reagent. After 5 mins., H_2SO_4 was added, and then an excess of KI aq. The liberated I was titrated with $Na_2S_2O_3$.

Amount of substance	0·1N-NaOCl, c.c.
10·0 c.c. 0·05N-Na N_2O_2	33·7 (6·7)
0·1 g. of $CaN_2O_2,4H_2O$	40·1 (6·9)
0·1 g. of $SrN_2O_2,5H_2O$	26·7 (6·3)
0·1 g. of $BaN_2O_2,4H_2O$	28·5 (7·7)

The figures in parentheses give atoms of active Cl per mol. of salt.

PART III.

Esters of Hyponitrous Acid.—Ethyl hyponitrite, prep. by Zorn (*Ber.*, 1878, **11**, 1630) by the action of $Ag_2N_2O_2$ on EtI in presence of dry ether, is described by him as a liquid, stable at room temp. but explosive at higher temps., having the normal vapour density [mol. formula $(C_2H_5)_2N_2O_2$] below 61°. He found that on reduction with Sn and HOAc

or HCl, or Na–Hg, traces of amino-compounds are formed. In presence of H_2O, the ester decomposed slowly at ordinary temps., rapidly at 40° and upwards, according to the equation $(C_2H_5)_2N_2O_2 = C_2H_5{\cdot}OH + CH_3{\cdot}CHO + N_2$.

Benzyl hyponitrite, described as fairly volatile at room temp., was prepared in a similar way by Hantzsch and Kaufmann (*Annalen*, 1896, **292**, 329); it decomposed similarly in presence of H_2O, forming Ph·CHO.

We describe the preparation of very pure silver hyponitrite, from which we prepared the ethyl, *n*-propyl, *n*-butyl, and benzyl esters by the same method, the first three being liquids and the last a solid. Cryoscopic determination of their mol. wts. in C_6H_6 solution showed them to possess the formula $R_2N_2O_2$. Attempts to determine the vapour density showed that even as low as 15° and at correspondingly low pressures, the liquid esters decompose, giving a gaseous product. A rapid determination of the vapour density of ethyl hyponitrite at 46° in the apparatus described below gave the value 46 (calc. : 59, H = 1).

Reduction of the esters with KOH and Devarda's alloy did not give any amino-compounds. The benzyl ester remained unchanged when treated with Al–Hg in alc. solution at room temp., but at higher temps. (60–70°), reduction to benzyl alcohol occurred. Since H_2O rapidly decomposes the ester at this temperature according to the equation :

$$(C_7H_7)_2N_2O_2 = C_7H_7OH + C_6H_5{\cdot}CHO + N_2 \qquad (1)$$

the aldehyde first formed is no doubt reduced to the alcohol.

The three liquid esters are readily decomposed by H_2O at 40° according to equation (1), but the benzyl ester only above its m. p. Even in presence of 50% KOH aq, the reaction appears to take the same course, since, after hydrolysis either at room temp. or at 0°, no hyponitrite can be detected.

The benzyl ester, when heated at 70—80° with an HOAc solution of phenylhydrazine, gave an 80% yield of

benzaldehydephenyl-hydrazone (m. p. 157°), so that even in acid solution the reaction takes the course of equation (1).

All the esters are unstable. The liquids on standing become slightly yellow, sometimes deep yellow, but the colour disappears on shaking. If the ester is kept for more than a week, however, the colour does not so disappear. The esters possess the normal cryoscopic mol. wts. even after a week, although the density of the liquid ethyl ester increases from 0·953 to 1·047. The benzyl ester becomes yellow and pasty, and after a week forms a liquid. On account of its low m. p. it is very difficult to prepare in hot weather.

Silver Hyponitrite.—Great care is necessary in the preparation of this salt, since otherwise the product is grey, or even black (cf. Divers, J., 1899, **47**, 97; Coblens and Bernstein, *J. Physical Chem.*, 1925, **29**, 750). 10 G. of $Na_2N_2O_2$ are dissolved in H_2O, the filtered solution made up to 200 c.c., and slightly less than the theoretical amount of 10% $AgNO_3$ aq. added drop by drop (stirring). If the solution is added rapidly, or a more conc. solution used, a considerable amount of a brown ppt. is formed, which requires vigorous shaking before it becomes pure canary-yellow. The ppt. is allowed to settle, the supernatant liquid is decanted, and divided into two equal parts. To one, the $AgNO_3$ solution is slowly added till the ppt. becomes *slightly* discoloured. The volume added is measured and the two portions mixed. An amount of $AgNO_3$ aq. 5 c.c. less than the amount required in the previous operation is then slowly added and the whole is mixed with the main ppt. and shaken. After the ppt. has settled, the liquid is decanted and 1% $AgNO_3$ aq. added until the colour of the liquid begins to change from bright yellow to pale yellow. This liquid is then shaken with the main ppt., and the remaining solid is washed 6—8 times by decantation, filtered off, and dried for 2—3 days in vac. over H_2SO_4 in the dark, during which it must retain its bright yellow colour. It is then powdered, and on standing over-night in a vac. desiccator over P_2O_5 it

becomes perfectly dry (Found : Ag, 78·1; N, 10·7. Calc. for $Ag_2N_2O_2$: Ag, 78·21; N, 10·16%).

Ethyl, n-*Propyl, and* n- *Butyl Hyponitrites.*—5-0 G. of EtI (or 5-5 g. of PrI, or 6-0 g. of *n*-BuI) are added to 20 c. c. of dry Et_2O in a freezing mixture, and 5-0 g. of dry powdered $Ag_2N_2O_2$ slowly added. The flask is closed with a cork carrying a $CaCl_2$ tube and left in the refrigerator for 24 hrs. The solution is filtered into a large test-tube, through which a current of dry air is slowly drawn until all smell of ether is removed, The ester is kept for 2 hrs, over anhyd. $CaCl_2$ and filtered, The esters cannot be distlled even at low pressures. The amount of nitrogen evolved on hydrolysis by H_2O showed them to be pure.

All the esters are easily sol, in EtOH, Et_2O, and C_6H_6, but practically insol. in H_2O, Ethyl hyponitrite when heated begins to decompose rapidly at 80—82° and explodes, but not very violently, whilst according to Zorn (*loc. cit.*) it is as explosive as NCl^3. The propyl and the butyl ester detonate when heated rapidly, but with slow rise in temp. the decomp. is smooth and without detonation.

Benzyl Hyponitrite·—From CH_2PhI (6·0 g,) and $Ag_2N_2O_2$ (4·5 g.), this ester is prepared as in the preceding cases, the ether being evaporated in a vac, over H_2SO_4. When nearly all the Et_2O has been removed, the solid is washed with dry light petroleum, redissolved in the minimum of dry Et_2O, and pptd. by the former solvent. It is then left on a porous plate in a partly evacuated desiccator containing H_2SO_4 and solid paraffin ; m. p. 48—49° (Found : N, 11·9. Calc. for $C_{14}H_{14}N_2O_2$: N, 11·57%).

Action of Aqueous Alcohol on the Esters.—A weighed amount of ester was dissolved in 10 c. c, of EtOH and diluted with H_2O to 25 c. c. in a flask fitted with two delivery tubes, one connected with a nitrometer and the other with a CO_2 generator. The flask was placed in a freezing mixture, and

the air expelled by a current of CO_2. The flask was then heated at 40—50°, or, in the case of the benzyl ester, at 70—75°. The gas collected was insol. in EtOH and was N. Gas evolution ceased after about 45 mins.

	Ester, g.	Gas at N.T.P., c.c.	N_2, % Found.	N_2, % Calc.
Ethyl hyponitrite ...	0·1205	22·0	22·83	23·73
" " ...	0·0937	17·1	22·82	
Propyl " ...	0·1180	17·5	18·54	19·18
Butyl " ...	0·1095	13·7	15·64	16·10
" " ...	0·0823	10·1	15·34	
Benzyl " ...	0·1020	9·0	11·04	11·57
" " ...	0·0923	8·2	11·11	
" " ...	0·1527	13·5	11·05	

Action of Phenylhydrazine on Benzyl Hyponitrite.—To 0·0677 g. of the ester, dissolved in EtOH, a solution of $NHPh{\cdot}NH_2$ in HOAc was added, the solution heated at 70—80° for 15 mins., and diluted with H_2O. The pptd. benzaldehydephenylhydrazone, 0·0426 g. (77·7% of theory), was recryst. from EtOH (m. p. 156—157°).

Hydrolysis of n-*Butyl Hyponitrite.*—0·5 G. of the ester was added to alc. KOH, the solution kept at room temp. for 5 hours, and then diluted with H_2O. The liquid had no smell of the ester. On addition of a little dil. $AgNO_3$ aq., only a brown ppt. was obtained, whereas yellow hyponitrite is first pptd. even in presence of a large excess of alkali. When the solution was left in the refrigerator, the smell of the ester could be detected after dilution for 3—4 days, but at no time, even after a week, when it no longer smelt of the ester, did the solution give any yellow ppt. with $AgNO_3$.

Reduction of Benzyl Hyponitrite by Aluminium Amalgam.—0·5 G. of the ester was dissolved in dil. aq. EtOH and 1 g. of freshly prepared Al-Hg added. After standing for ½ hr. at room temp., the solution was poured into a large vol. of H_2O and extracted with Et_2O; the extract on evaporation at reduced press. deposited unchanged benzyl hyponitrite. When

the solution was kept at 60° for ½ hr., the ethereal extract gave a non-nitrogenous liquid, b. p. 240°, *viz.*, benzyl alcohol.

Reduction of Ethyl Hyponitrite by Devarda's Alloy.—About 1 g. of the ester was added to 25 c. c. of 50% KOH solution with 2 g. of Devarda's alloy. The distillate was very slightly alk. (requiring 0·1 c. c. of 0·1*N*-HCl) and showed a trace of NH_3. It gave no carbylamine test.

Vapour Density.—In the determination with ethyl hyponitrite in the Hofmann apparatus, the mercury column, on cooling, did not return to the original level, indicating decomp. at the reduced press. The modified Hofmann apparatus shown in Fig. I (See J. C. S. 1932, 2595) was then used in an attempt to determine the vapour pressure, but the instability of the esters renderedit useless in this case. The tube A is filled with dry Hg, and a small amount of substance introduced into it. It is then transferred in a deep mercury trough to the tube B, and the rubber stopper pressed in. The whole apparatus is then immersed in a water-bath. When the bath attains the desired temp., B is connected with a Sprengel pump. When the mercury in A begins to fall, the pump is stopped and the manometer reading taken. The difference (*d*) in the mercury levels is measured by a cathetometer and, after temp. correction, is added to the manometer reading. After each reading the vac. can be released, whereupon, if no decomp. occurs, no gas will be found in A.

For the determination of vapour density A is substituted by a 50-c. c. flask as shown dotted. After the apparatus has been heated to the desired temp., the pump is started, and the Hg in the neck of the flask adjusted to the graduation mark. Decomp. can be detected as in the previous case,

Molecular weights of the esters in benzene solution.

Ethyl hyponitrite (M=111).

C_6H_6 = 13·26 g.

w.	*d.*	*M*
0·0468	0·151°	119·9
0·0964	3·322	115·8
0·1286	0·429	116·1
		Mean 117·3

Propyl hyponitrite (M=145).

C_6H_6 = 13·15 g.

w.	*d.*	*M.*
0·0281	0·076°	144·2
0·0658	0·179	143·4
0·0469	0·121	151·2
		Mean 146·3

Butyl hyponitrite (M=174).

C_6H_6 = 13·50 g.

0·0577	0·127	172·6
0·0643	0·140	174·6
0·1030	0·226	173·2
		Mean 173·5

Benzyl hyponitrite M=242).

C_6H_6 = 1427 g.

0·0813	0·121	241·5
0·0602	0·089	243·2
0·0907	0·135	241·5
		Mean 242·1

Measurements of the parachors and dipole moments of the esters, and the dipole moment of nitramide, have been made and will be published. The parachors of the esters are not in agreement with the usual formula if the usual values for the constants are used, but the dipole moments show that the formula RO·N : N·OR is very probably correct. The dipole moment of nitramide is large and throws some light on its constitution.

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East London College.
University of London.

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XXXV—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XII. Decomposition of Quaternary Ammonium Alkoxides.

By C. K. Ingold and C. S. Patel,

Previous studies of quaternary ammonium compounds have shown that the proportion in which thermal decomposition proceeds according to the reaction (B) whereby a radical from the cation appears in association with the anion, or according to the alternative reaction (A), in which a radical from the cation is eliminated as an olefin, is strongly dependent on constitutional influences. In particular it is known that a general change in reaction-direction in the sense B$\longrightarrow$ A is observed on passing from an ammonium compound with a very feebly basic anion such as chloride towards one in which the anion has the strong basicity of the hydroxide ion, the cation being the same throughout. The hydroxide ion is the most basic of those hitherto investigated in this connexion, and the present experiments were undertaken in order to determine whether the aforesaid change in the direction of decomposition continues to progress in the same sense when the basicity of the anion is further increased, beyond that of hydroxide, to that of methoxide and ethoxide.

According we have prepared trimethylethylammonium and trimethyl*iso*butylammonium methoxide and ethoxide. The four compounds decompose to give, on the one hand ethylene or *iso*butylene, and on the other a methyl or an ethyl ether, together with the complementary amine in each case (cf. Achmatowicz, Perkin, and Robinson, J., 1932, 500) The proportion of reaction A, far from being notably greater than in the case of the ammonium hydroxides, was actually a few units % smaller (Table), and it appears that the replacement of reaction B by reaction A on increasing the basicity of the anion of the ammonium compound does not continue for anions more basic than hydroxide.

The Principal products of decomposition of benzyltrimethylammonium ethoxide are trimethylamine and benzyl ethyl ether.

Table : Percentage of Reaction A.

Cation.	Anion.........OH^{--}	OMe^{--}.	OEt^{--}.
$C_2H_5 \cdot NMe_3$	94	90	88
iso-$C_4H_9 \cdot NMe_3$	63	57	55

Experimental.

Ethyl- *iso*butyl-trimethylammonium bromides (0·1 g.-mol.) were converted *via* the hydroxides into the chlorides, which after thorough drying were added to an equiv. of a solution of NaOMe or NaOEt in the appropriate Ca-dried alcohol. After filtration of the NaCl with precautions against access of moisture the solutions were completely distilled through the following train, *viz.*, a condenser, a cooled flask containing dil. HCl, a reflux condenser, a second flask of dil. HCl, a second reflux condenser, a cooled flask containing Br, a second similar flask, a drying-tube, and an aspirator. At the end of the dissillation the apparatus was swept through with 10 vols. of dry air whilst the liquid in the HCl traps was kept gently boiling under reflux. The excess of Br was destroyed with ice and SO_2, and the olefin bromide extracted with light ligroin, washed with $NaHCO_3$ aq. and H_2O, distilled. The figures in the two right hand columns of the table are based on concordant triplicate determinations of the yield of olefin bromide, and the figures under the heading OH—are taken from Ingold and Vass's data (J., 1928, 3125). Amines and ethers could not be isolated quantitatively.

Benzyltrimethylammonium ethoxide prepared from the directly formed chloride, yielded 65% of rectified benzyl ethyl ether b. p. 185°, a large amount of trimethylamine, and a small amount of a less volatile base, presumably benzyldimethylamine.

The University, Leeds.

University College, London.

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XXXVI—Influence of Poles and Polar Linkings on the Course pursued by Elimination Reactions. Part XVI. Mechanism of the Thermal Decomposition of Quaternary Ammonium Compounds.

By E. D. Hughes, C. K. Ingold, and C. S. Patel

Although the general theory of the two main modes of decomposition of quaternary ammonium compounds

$$R^1R^2CH\cdot CR^3R^4\cdot\overset{+}{N}R'R''R'''\}\overset{-}{X}\longrightarrow$$
$$R^1R^2C{:}CR^3R^4 + NR'R''R''' + HX \qquad (A)$$
$$(R\cdot\overset{+}{N}R'R''R'''\}\overset{-}{X}\longrightarrow$$
$$RX + NR'R''R''' \qquad (B)$$

has not been treated in this series since the appearance of Part I Hanhart and Ingold, J., 1927, 997), yet the point of view underlying the more recently recorded experiments has developed appreciably in the meantime.

Reaction (*A*).—The conception of reaction (A) advanced in Part I may be symbolised as follows :

$$\begin{array}{l} H\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\overset{-}{X} \\ | \\ R^1R^2C\longrightarrow CR^3R^4\longrightarrow\overset{+}{N}R'R''R'''\longrightarrow \\ R^1R^2C{:}CR^3R^4 + NR'R''R''' + HX \qquad (A2) \end{array}$$

The equation depicts, first, predisposition towards reaction arising from the incipient ionisation of the β-hydrogen atom induced by the electron-attraction of the ammonium pole; and secondly, the actual process whereby the β-proton is attracted by the anion with the assistance of octet-preserving displacements of electron-duplets towards the pole of the cation. Wide variations in the structure of the ammonium compound have been shown to affect the reaction in the manner demanded by this mechanism.

The above description requires that reaction (A) be of the first order with respect to each of the participating ions and therefore of the second order with respect to the ammonium compound. The numerical part of the description (A2) is intended to symbolise this dynamical character (*vide infra*).

In part XV (preceding paper) it is shown that the dynamics of the decomposition of β-phenylethyltrimethylammonium hydroxide (reaction A) conform to the requirements of mechanism (A2); and we regard this demonstration as indirect evidence that second-order dynamics govern the decomposition (reaction A) of all ammonium compounds in which the incipient ionisation of the β-hydrogen atom is not greater, and the basicity (proton-affinity) of the anion is not less, than in β-phenylethyltrimethylammonium hydroxide. For example, the formation of any purely aliphatic mono-olefin from a quaternary ammonium hydroxide or alkoxide (Part XII, this vol., P 68.) may be considered to proceed according to mechanism (A2).

Starting from any of the ammonium compounds referred to in the last paragraph, we now imagine progressive changes of structure which (*a*) increase the hydrogen-polarisation in the cation, and (*b*) decrease the proton-affinity of the anion. Evidently a state will ultimately be reached in which the anion (*a*) is not required, and (*b*) is structurally unable, to assist effectively in the extraction of the β-proton. In these circumstances reaction (A) must be a two-stage process such that the cation and anion are concerned in separate stages :

$$R^1R^2\overset{\overset{\displaystyle H}{|}}{C}\text{——}CR^3R^4\text{——}\overset{+}{N}R'R''R''' \longrightarrow$$

$$\left.\begin{array}{l} R^1R^2C{:}CR^3R_4 + NR'R''R''' + \underset{\text{(solvent)}}{\overset{+}{H}_{\text{solvated}}} \\ \overset{+}{X} + \overset{+}{H}_{\text{solvated}} \rightleftharpoons HX + \text{solvent} \end{array}\right\} \quad (A1)$$

Thus we are led to envisage a second mechanism, here designated (A1), which is of first order with respect to the cation, of zero order with respect to the anion, and thus of order unity with respect to the ammonium compound.

Examples illustrating this mechanism are given in Part XV (*loc. cit.*), Starting from β-phenylethyltrimethylammonium hydroxide, the hydrogen-polarisation in the cation is increased by the introduction of a nitro-group and the basicity of the anion is decreased by replacing it by a halide ion. The decompositions (reaction A) of the resulting β-*p*-nitrophenylethyltrimethylammonium bromide and iodide were each found to be unimolecular with respect to the appropriate salt, and both salts gave the same velocity coefficient.

In relation to these examples, the first stage of mechanism (A1) may require subdivision by the introduction of a hypothetical, and presumably unstable, intermediate betaine; the ammonium cation would then be regarded as a definite acid of which the betaine is the conjugate base and the immediate precursor of the olefin:

$$R^1R^2CH{\cdot}CR^3R^4{\cdot}\overset{+}{N}R'R''R''' \rightleftarrows$$

$$R^1R^2\overset{-}{C}{\cdot}CR^3R^4{\cdot}\overset{+}{N}R'R''R''' + \overset{+}{H}_{\text{solvated}}$$

$$R^1R^2\overset{-}{C}\text{——}CR^3R^4\text{——}\overset{+}{N}R'R''R''' \longrightarrow$$

$$R^1R^2C{:}CR^3R^4 + NR'R''R'''$$

If k_1 and k_2 are velocity coefficients representing respectively the rate of dissociation and of formation of the acid, whilst k_3 similarly specifies the speed of fission of the base, then the experimental unimolecular coefficient, k, has the form, $k_1k_3/(k_2[\mathrm{H}^{\cdot}]+k_3)$. A definite dependence of k on $[\mathrm{H}^{\cdot}]$ has been observed and its direction is consistent with the formula given. This is the reason for the suggested sub-division, which, however, is not regarded as necessarily a general feature of mechanism (A1).

Thus the original conception of reaction (A), represented in mechanism (A2), is now generalised by the contemp lation of a graded range of mechanism, (A2)—(A1), of which the extremes have been illustrated.

Reaction (*B*).—In the representation of this reaction advanced in Part I (*loc. cit.*) two stages are distinguished : it is assumed that the cation suffers fission without the direct intervention of the anion, which only subsequently unites with the ejected radical :

$$\left.\begin{array}{l} R{-}\overset{+}{N}R'R''R''' \longrightarrow \overset{+}{R} + NR'R''R''' \\ \quad\;\; \overset{+}{R} + \overset{-}{X} \longrightarrow RX \end{array}\right\} \ldots \quad \ldots \text{(B1)}$$

This mechanism, designated (B1), represents a reaction which is of first order with respect to the cation, of zero order with respect to the anion, and therefore of first order with respect to the ammonium compound. It has afforded a consistent explanation of many phenomena. but recent investigation, both by von Braun and his collaborators and by ourselves, has revealed four difficulties in its general application.

First, von Braun *et al.*, studying the decomposition of trimethyl-*n*-decylammonium hydroxide in dilute solution at constant volume, found that the ratio of the quantities of methyl alcohol and decylene eliminated in the same experiment did not depend on the initial concentration of the ammonium hydroxide (*Annalen*, 1929, **472** 121; *cf. Ber.*, 1931 **64**, 2610). This result shows thst reaction (A) and (B) are, in this instance of the same order, but it does not determine the order. We combine it, however, with our dynamical study of reaction (A) (Part XV, *loc. cit.*), which as the previous section shows, requires the elimination of decylene to be bimolecular. It follows that the elimination of methyl alcohol is bimolecular, contrary to the reaction order required by mechanism. (B1).

Secondly, an investigation into the decomposition of benzhydryltrimethylammonium hydroxide in dilute solu-

tion at constant volume has shown (Part XIII, this vol., p. 69) that the ratio of the quantities of benzhydrol and methyl alcohol eliminated in the same experiment is strongly dependent on the initial concentration of the ammonium hydroxide. The ratio is also changed by the initial addition of extraneous hydroxide ions. Both results are indicative of the existence of simultaneous reactions of different orders, and a satisfactory interpretation was found to follow from the assumption that the elimination of benzhydrol and methyl alcohol are reactions of the first and second order respectively Once again the elimination of methyl alcohol exhibits dynamics contrary to the demands of mechanism (B1).

The third difficulty is that, although until recently all the available observations concerning the relative facility with which those groups which cannot appear as an olefin become eliminated as alcohols from quaternary ammonium hydroxides were consistent (Part I, *loc. cit.*) with mechanism (B1), yet one clear case contrary to this mechanism has been observed (Part XI, this vol., p. 67) in the exclusive formation of methyl alcohol and the complementary amine from trimethyl-*neo*pentylammonium hydroxide; for mechanism (B1) requires that the group with the greater tendency to separate as a cation should preferentially be eliminated as alcohol, and evidently electron-release from the *tert.*-butyl portion of the *neo*pentyl radical should facilitate the formation of the corresponding cation, wherefore *neo*pentyl alcohol rather than methyl alcohol should have been eliminated.

The fourth and last point has reference to the widely observed phenomenon that, when the decomposition of an ammonium salt with a feebly basic anion (*e.g.*, a choride) is compared with that of a corresponding compound having the same cation but a much more strongly basic anion (*e.g.*, the hydroxide), reaction (A) assumes considerably greater relative importance in the latter case. This is consistent with the operation of the combination of mechanisms (A2)

and (B1) (cf. Part I, *loc. cit.*), and whilst the hydroxide ion remained the most basic of those investigated in this connexion no difficulty with this interpretation arose. But an extension of the comparision by the inclusion of alkoxide ions (Part XII, this vol,, p, 68) has revealed that the suppression of reaction (B) in favour of (A) does not continue when the basicity of the anion is increasen beyond that of the hydroxide ion. This effect cannot be ascribed to the operation, over the extension in the range of anions, of the combination of mechanism (A1) and (B1), for it will be clear from the preceding section that any increase in the basicity of the anion must tend to strengthen the retention of mechanism (A2). The effect referred to must therefore be attributed to some failure of mechanism (B1).

Commencing with any case to which mechansim (B1) applies, let us imagine changes of structure which (*a*) decrease the cationic stability of the eliminated group, and (*b*) increase the basicity, or, more generally, the nucleophilic tendencies, of the anion. Eventually a state must be reached in which the intervention of the anion (*a*) is necessary for, and (*b*) is effective in, the elimination of the group. The process will now occur in once stage as in the scheme ;

$$\{R'R''RR'''\overset{+}{N}—R\}\overset{-}{X} \longrightarrow R'R''R'''N + RX \qquad (B2)$$

According to this mechanism reaction (B) is of the first order with respect to each ion, and hence bimolecular with respect to the ammonium compound, wherefore the mechanism receives the designation (B2). Thus arises the possibility of a generalisation of the mechanistic theory on the lines already illustrated in relation to reaction (A).

Before pursuing this conception, it is necessary to refer to the alternative suggestion by von Braun *et al.* (*loc. cit.*) that reaction (B) is a decomposition of the un-ionised ammonium hydroxide molecule :

$$\{RR'R''R'''\overset{+}{N}\}\overset{-}{OH} \rightleftarrows$$
$$RR'R''R'''N{\cdot}OH \longrightarrow$$
$$R{\cdot}OH + R'R''R'''N \qquad (B')$$

Two series of special experiments, relating to the decomposition of trimethyl-*n*-decyl-ammonium hydroxide, were held to support this view. First, it was found that the addition of glycerol to the ammonium hydroxide decreased the proportion of decylene formed and thus augmented the proportion of methyl alcohol; and it was argued that the glycerol, by repressing the ionisation of the ammonium hydroxide, should favour the molecular reaction (B) at the expense of the ionic reaction (A), though possible disturbance through the formation of ammonium glyceroxides was admitted. Secondly, it was observed that the addition of potassium hydroxide increased the proportion of decylene and decreased that of methyl alcohol; and the argument on this point was that, although extraneous hydroxide ions, by repressing ionisation, must fecilitate reaction (B), yet, becuase the consentration of molecular ammonium hydroxide is in any circumstances small, therefore this effect must be small in comparison with the direct, accelerative effect of the added hydroxide ions on the ionic reaction (A).

We accept Sidgwick's principle whereby the formation of an un-ionised quaternary ammonium hydroxide is impossible, and accordingly regard all decompositions of ammonium compounds as exclusively inonic. Concerning the effect of added glycerol, we concur in the suggestion relating to the formation of glyceroxides. Regarding the effect of added potassium hydroxide we would remark, first, that the argument based on this effect is contrary to the mass law, and secondly, that von Braun and his co-workers themselves have shown that in aqueous solution reactions (A) and (B) are *equally* affected by hydroxide ions. Furthermore, we imagine that the un-ionised molecule is expected to be more plentiful in the fused ammonium hydroxide than in dilute

aqueous solution; wherefore, according to scheme (B'), the proportion of reaction (B) might be expected to be greater in the former case, contrary to the observations, The foregoing comments will not obscure the circumstance that von Braun's scheme (B') requires the same reaction order as our scheme (B2).

Returning to the considertion of mechanism (B2), we first observe that, in each of the cases in which the application of scheme (B1) hes led to inconsistencies, the *ad hoc* introduction of its alternative (B2) would interpret the observations. It provides the dynamics which are required in relation to the elimination of methyl alcohol. It accords with reaction inhibition by electron release, and thus interprets the case of the *neo*pentyl group ($Me_3C \longrightarrow CH_2\cdot$), since polarisation in this direction must oppose the address of the anion. Also, mechanism (B2), like (A2), depends on the basicity of the anion, and this circumstance accommodates the observed absence of any marked change in the direction of decomposition on replacing the hydroxide ion by the more basic alkoxide ion.

On the other hand, it is equally evident that no *general* application of mechanism (B2) is possible; for the reasons which led originally to the proposal of mechanism (B1) still hold, and in addition we now have direct evidence for unimolecular dynamic in the elimination of benzhydrol, and indirect evidence for the same mechanism in the case of the elimination of triphenylcarbinol (Huges, Part XIV, this vol., p. 75). Both mechanisms must be envisaged [this was done in Part I, but (B2) was not regarded as important].

The circumstances which theoretically should determine the replacement of one of these mechanisms by the other are clear, In the molecule $\{RR'R''R'''\overset{+}{N}\}\overset{-}{X}$, if either (*a*) the cationic stability of R is progressively increased, or (*b*) the basicity of $\overset{-}{X}$ is progressively decreased, then a stage should be reached at which mechanism (B2) becomes superseded by

(B1). It remains to show that this theoretical relation corresponds to known experimental data.

The effect of changes of type (a) in the cation may be illustrated first by reference to alkyl groups. Concerning the series $CH_3\cdot$, $AlkCH_2\cdot$, $Alk_2CH\cdot$, $Alk_3C\cdot$, it is known that methyl and *tert*-butyl groups are readily eliminated as alcohols from quaternary ammonium hydroxides, whilst primary and secondary alkyl groups are not (cf. Parts I and XI, *locc. cit.*); thus the property of facile elimination in the form of alcohol passes through a minimum in the series considered.

The circumstance may be interpreted as follows. From left to right in the series the inductive effect of the alkyl components produces a progressive increase of electron density at the point of attachment of the whole group. This electron density is lowest in the methyl group and it is consistent that this group suffers elimination by mechanism (B2). As explained in connexion with the *neo*pentyl group, the first effect of the introduction of alkyl components in place of hydrogen is to suppress reactivity by mechanism (B2), and, apparently, one alkyl substituent is sufficient to render it immeasurably small. Mechanism (B1), however, as is evident from its nature, must be facilitated by alkyl substitution, so that at some stage in the series reactivity by this alternative mechanism should rise, to an appreciable value; and once this mechanism takes control of the decomposition, further alkyl substitution must enhance reactivity. This explains the minimum occurring in the series, and we expect similar conditions to apply in analogous substitution reactions such as the alkaline hydrolysis and alcoholysis of alkyl halides.

The corresponding theory of the aralphyl series $CH_3\cdot$, $ArCH_2\cdot$, $Ar_2CH\cdot$, $Ar_3C\cdot$ is different because the polar effect of the phenyl substituent is electromeric and duplex, and this

group thus adjusts itself to the requirements of the system. In mechanism (B2) it is difficult to state what those requirements are, since at the moment of reaction the aromatic electrons are simultaneously under the opposing influences of the ammonium pole and the attracted anion. In mechanism (B1), however, an integral cationic charge requires dispersal, and accordingly electron release from the aryl groups must be maximal. Hence in reaction by mechanism (B2) progressive substitution by aryl groups is expected to produce comparatively small effects (in either direction), but in reaction by mechanism B1) each additional aryl group should greatly enhance reactivity. Thus, this series also should contain a point at which mechanism (B1) supplants (B2). The point of supersession need not, however, be associated with minimal reactivity, but it should have the property that the portion of the series to its left should show slight (possibly irregular) effects, and that to its right a large enhancing effect, of the aryl groups on reactivity.

In the series, CH_3, CH_2Ph, $CHPh_2$, CPh_3, observations are available (cf. Parts XIII and XIV, *locc. cit.*), and the preceding statement faithfully describes them. The point of supersession occurs at $CHPh_2$, and, independently of the indication provided by the observed differences of reactivity, the alteration of mechanism is clearly established by dynamical evidence. The expectation that similar conditions will prevail for other aliphatic substitutions such as the alkaline alcoholysis or hydrolysis of corresponding halides is supported by the observation (Ward, J., 1927, 2285) of a change from second- to first-order dynamics in this reaction on passing from a benzyl to benzhydryl chloride.

Effects of type (*b*) to be expected from changes in the anion may be illustrated by means of a series such as OEt', OH', OPh', OAc', Cl', the order being that of decreasing basicity. In general, there will be a point such that, to its left mechanism (B2), and to its right mechanism (B1), controls reaction (B). Assuming that a simultaneous reaction

(A) is controlled by mechanism (A2) throughout then to the left of the point of mechanistic replacement both reactions (A) and (B) are similary dependent on the anion, changes in which will not much alter the direction of decomposition, whilst to the right of the same point reaction (A) alone will depend on the anion, a decrease in the basicity of which should therefore favour reaction (B). The above will be recognised as a description of the corresponding observations (cf. Parts I and XII), which formerly could not be reconciled.

When the various series can be more fully filled in, what has been described as a "point" of mechanistic change will probably appear as a region, and thus, just as with reaction (A), we now generalise the original conception of reaction (B) by the contemplation of a range of mechanisms, (B1)—(B2), both extremes of which have been experimentally exemplified. Most aliphatic substitutions can with advantage be regarded analogously, and the lines along which this further generalisation would proceed will become evident on comparing the foregoing with a previous discussion of aliphatic substitutions in the side chains of aromatic compounds (Ingold and Rothstein, J., 1928, 1217; cf. Ingold and Patel, J. *Indian Chem. Soc.*, 1930, 7 95).

University College, London.

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XXXVII.—Interaction of Selenium Oxychloride with the substituted Amides of Malonic Acid.

By R. K. Trivedi.

Ever since the study of the nature of the hydrogens of the reactive methylene (CH_2) group situated between two negative groups was undertaken in these laboratories, efforts have been made to replace these hydrogens of the reactive methylene group by various groups and to study the effect of the adjacent radicals on such replacements. The chlorides of sulphur gave many fruitful results. Sulphur monochloride gave dithioketones and dithioethers, (Naik, J. C. S. T. 1921, *119*, 379-1166); while sulphur dichloride yielded compounds of the type

R. NH. CO╲ ╱SCl
C
R. NH. CO╱ ╲SCl

(Naik & Jadhav, J. I. C. S. 1926, 3, 260).

Reactions with Thionyl chloride also gave two types of products:

(i) Sulphoxides
and (ii) (Sulphidea. (Naik & Parekh, J. I. C. S. 1930, 7, 145).

From the study of these interactions it was expected that the chlorides of selenium, being of a nature similar to that of sulphur chlorides, would also react in a similar manner. A study of the interaction of selenium tetrachloride with substances containing reactive methylene group or a substituted methylene group revealed the formation of the selenides of the type :—

R. NH. CO╲ ╱CO. NH. R.
C : Se : Se : C
R. NH. CO╱ ╲CO. NH. R.

(Naik & Trivedi, J. I. C. S., 1930, 7, 239.)

In the present study it was thought interesting to study the interactions between selenium oxychloride ($SeOCl_2$) and substances containining the reactive methylene group situated between two carbonyl groups. For these purpose the following substances were selected :—

(1) Malonanilide $(C_6H_5NH.\ CO)_2CH_2$

(2) Malon-diorthotolyl amide. $(C_7H_7NH.\ CO)_2CH_2$-ortho.

(2) Malon-diparatolyl amide. $(C_7H_7NH.\ CO)_2CH_2$-para.

It was expected that as in the case of the interaction of these substances with thionyl chloride (Naik & Parekh, loc. cit) this reaction would also yield the Selenoxides of the type :—

$$\begin{array}{l} R.\ NH.\ CO\diagdown \\ \qquad\qquad\quad C : Se : O \\ R.\ NH.\ CO\diagup \end{array}$$

The corresponding sulphoxides obtained by Naik & Parekh (loc. cit.) were given the structure

$$\begin{array}{l} R.\ NH.\ CO\diagdown \\ \qquad\qquad\quad C : S : O \\ R.\ NH.\ CO\diagup \end{array}$$

Accordingly, the reaction of selenium oxychloride with malonanilide was studied at the outset. Selenium oxychloride and malonanilide in anhydrous ether at room temperature gave dichlor-malonanilide and selenium as follows :—

$$\begin{array}{l} C_6H_5NH.\ CO\diagdown \\ \qquad\qquad\qquad CH_2 + SeOCl_2 = \\ C_6H_5NH.\ CO\diagup \end{array} \begin{array}{l} C_6H_5NH.\ CO\diagdown \\ \qquad\qquad\qquad CCl_2 + H_2O + Se \\ C_6H_5NH.\ CO\diagup \end{array}$$

In boiling anhydrous benzene the reaction proceeded in a different way and the product obtained was identified as mesoxanilide m. p. 191°C. This subtance has also been obtained by J. U. Nef (J. C. S. A., 1892, 62, 1440). The interaction could be represented as taking place in two stages : At first the selenoxide is formed :

$$\begin{array}{l} C_6H_5NH.\ CO\diagdown \\ \qquad\qquad\qquad CH_2 + SeOCl_2 = \\ C_6H_5NH.\ CO\diagup \end{array} \begin{array}{l} C_6H_5NH.\ CO\diagdown \\ \qquad\qquad\qquad C : Se : O + 2HCl \\ C_6H_5NH.\ CO\diagup \end{array}$$

(1) Malonanilide-selenoxide.

In the next stage the substance (1) seems to decompose as under :—

$$\left.\begin{array}{l} C_6H_5NH.\ CO \\ C_6H_5NH.\ CO \end{array}\right\rangle C : Se : O = \left.\begin{array}{l} C_6H_5NH\ CO \\ C_6H_5NH.\ CO \end{array}\right\rangle C : O + Se$$

(II) Mesoxanilide.

That the substance (I) may decompose to give rise to (II) is not surprising in view of the experimental conditions, as also in view of the fact that the selenoxide is more unstable than the corresponding sulphoxide. This is also supported by an observation viz., ..." the selenium atom is far more labile than the sulphur atom in the corresponding thiocompounds." (Schmidt, Ber., 1921, *54* (*B*; ,2067-2070).

The interaction of malondiorthotolylamide and malondiparatolylamide with selenium oxychloride followed the same course giving rise to the respective mesox-derivatives as follows :—

$$\left.\begin{array}{l} C_7H_7NH.\ CO \\ C_7H_7NH.\ CO \end{array}\right\rangle CH_2 + SeOCl_2 = \left.\begin{array}{l} C_7H_7NH.\ CO \\ C_7H_7NH.\ CO \end{array}\right\rangle C:O + 2HCl + Se$$

EXPERIMENTAL.

(*i*) *Interaction of malonanilide with Selenium oxychloride*:

Equimolecular quantities of selenium oxychloride and the amide were kept suspended in 50 c. c, s of anhydrous ether prepared by distilling it over sodium as well as over phosphorus pentoxide. The amide went into solution very slowly and during the interaction hydrogen chloride was found to evolve imperceptibly, after standing for 24 hours the dark red reaction mixture deposited fine silky needles. This reaction product (in the case of malonilide) was purified when fine white needles were obtained. On analysis and further identification these were revealed to be the crystals of dichloromalonanilide, m. p. 127°C. (Naik & Shah, J. I. C. S., 1927, 4, 11). The mother liquor was allowed to stand for a few days more but nothing separated out except

a film of grey, metallic selenium. The reaction seems to take place as represented on page (298)

It was then thought interesting to revise the experimental conditions to see if such a revision secured different results. The reaction was, accordingly, carried out in boiling anhydrous benzene solution with equimolecular quantities (Malonanilide 5 gms. and selenium oxychloride 2.5 gms.) of the reactants as in the previous case. After refluxing for 24 hours a dark red solution of the reaction product was obtained. This was concentrated and was then added dropwise into a large amount of petroleum. A resinous red product was precipitated. This was isolated from the benzene-petrol mixture and was redissolved in benzene. This solution was refluxed with freshly reduced copper-gauze in order to remove the free selenium which might inhibit the crystallisation of the pure substance. The pure product was obtained after six such attempts at purification. The product was found to be a pale yellow microcrystalline powder with m. p. 191°C Selenium as well as chlorine were found to be absent in this product. On analysis and further identification this substance was found to be mesoxanilide, (Nef, J. C. S. A., 1892, *62*, 1410; Annalen, *270*, 267–335). The product obtained herein combines readily with water and with alcohol to form colourless hydrate and alcohol respectively. It also combines with phenyl hydrazine in dry benzene solution. All these reactions are shown by the mesoxanilide m. p. 190°C. obtained by Nef (loc. cit). [Found; C : 67.06; H, 4.49; and N, 10.5; $C_{15}H_{12}N_2O_3$ requires C 67.16; H, 4.48 and N. 10.45.

The mixed melting points of the products as prepared by Nef's (loc. cit) method and as prepared as described herein confirms the identity of the product obtained herein.

(II) Interaction of Malondiorthotolylamide with selenium oxychloride :

The reactants were taken in eqimolecular quantities as in the previous case and the reaction product was obtained in

exactly the same way as described above. It was obtained after purification in the form of yellowish micro-crystalline powder melting at 172°C. [Found : C, 68.85; H, 5.5; and N, 9.5; C_{17} H_{16} N_2 O_3 requires C, 68.9 H, 5.4 and N, 9.46.]

The substance gave a hydrate on boiling with water. This hydrate was obtained in the form of colourless needles which turned yellow at 100°C, and melted at 127–130°C. with decomposition. It turns blue litmus red and is soluble in dilute solution of sodium carbonate

(III) Interaction of malondiparatolylamide with selenium oxychloride.

Mesoxdiparatolylamide was prepared in exactly the same way as the corresponding ortho.derivative. The pure product melted at 187°C. [Found C, 68.8; H, 5.35; and N, 9.55; C_{17} H_{16} N_2 O_3 requires C, 68.9; H, 5.4 and N, 9.46.]

The product when boiled with water gives a hydrate which is obtained in the form of colourless needles melting with decomposition between 122—130°C. Mesoxdiparatoluidide hydrate. C $(OH)_2[C(OH): N. C_6 H_4 Me]_2$ melts between 120, 130°C, (W. R. Smith, Amer. Chem. 16. 372; 393; J. C. S. A. 1894, 66, 407).

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Chemistry Department,
The College, Baroda.

Uber Einige Neue Abbauprodukte Des Digitogenins

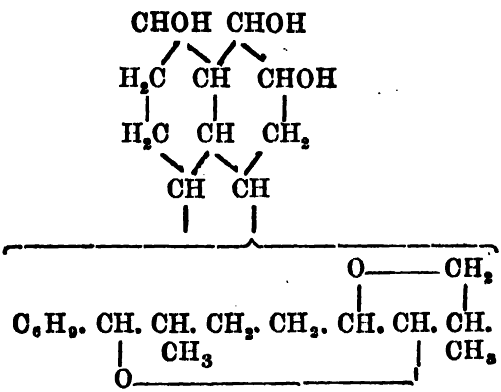
von

A. WINDAUS AND S. V. SHAH

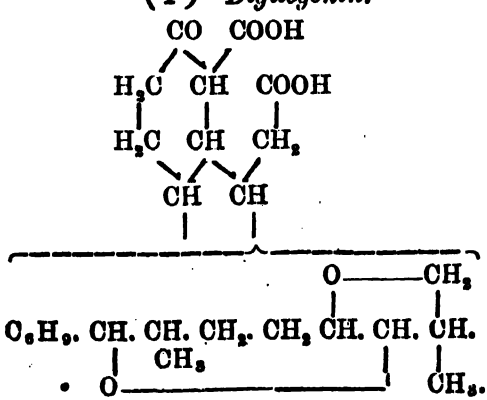
In Anschluss an fruhere Versuche von Kiliani[1] haben wir die Einwirkung von Salpetersaure auf Derivate des Digitogenins (I) studiert und zunachst die Digitosaure (II) and die Oxydigitogensaur (VII) mit diesem Oxydationsmittel behandelt.

(I) Einwirkung von Salpetersaure auf Digitosaure

Digitosaure ist eine Ketodicarbonsaure von der Formel $C_{26}H_{38}O_7$, sie enthalt noch 3 hydrierte Ringe, 2 Carboxylgruppen, 1 Ketogruppe and 2 oxydartig gebundene Sauerstoffatome.

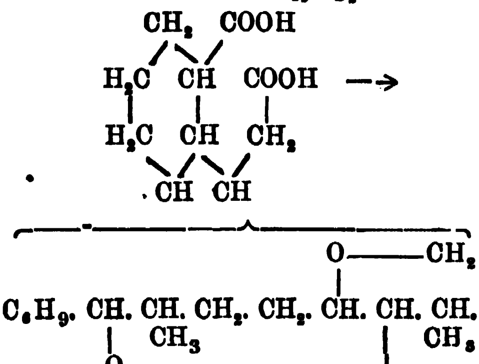


(I) *Digitogenin.*

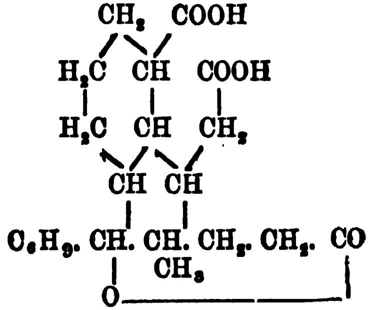


(II) *Digitosaure.*

Digitosaure liefert bei der Oxydation mit Salpetersaure eine schön krystallisierte Saure, die vier Kohlenstoffatome weniger enthalt als das Ausgangsmaterial and die Formel $C_{22}H_{31}O_{10}N$ besitzt; sie gibt einen krystallisierten Dimethylester, in der Kalte titriert sie sich zweibasisch, beim Erwarmen mit Alkalien spaltet sie salpetrige Saure und vielleicht auch Salpetersaure ab and geht in harzartige Produkte uber; bei der Oxydation mit Kaliumpermanganat gibt sie eine neue Saure, die sich als dreibasisch erweist und vielleicht die Formel $C_{22}H_{30}O_{10}$ besitzt. Es ist nicht moglich, auf Grund dieser Befunde den Verlauf der Reaktion klar zu ubersehen. Bemerkenswert ist es aber, dass auch die Gitogensaure (III) beim Erwarmen mit Salpetersaure 4 Kohlenstoffatome abspaltet; diese Abspaltung erfolgt aus der Seitenkette und fuhrt zu einem Lacton $C_{22}H_{32}O_6$ (IV).

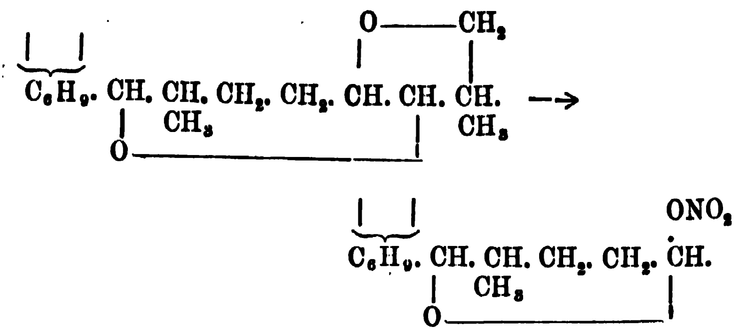


(III) *Gitogensaure.*



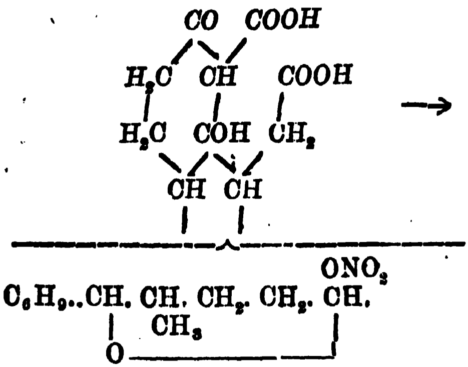
(IV) *Lacton $C_{22}H_{32}O_6$*

Es ist wahrscheinlich, dass auch die 4 Kohlenstoffatome, die aus der Digitosaure abgespalten werden, aus der Seitenkette stammen; hierbei entsteht aber kein Lacton, sondern, wie es scheint, ein Ester der salpetrigen Saure oder der Salpetersaure. Wir haben uns lange um eine Deutung dieser Reaktion bemuht und sind zu der Vermutung gekommen, die neue Verbindung $C_{22}H_{31}O_{10}N$ sei der Salpetersaureester eines Lactols. Der Abbau der Seitenkette ware dann folgendermassen zu formulieren :

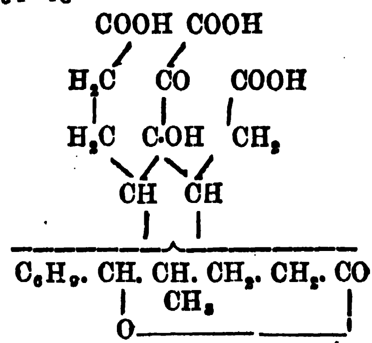


Allerdings kann sich die Oxydation nicht auf diesen Vorgang beschranken, da das Reaktionsprodukt dann nur 9 Sauerstoffatome enthalten wurde, wahrend die richtige Formel $C_{22}H_{31}O_{10}N$ lautet. Vermutlich wird gerade wie beim Ubergang der Oxydigitogensaure $C_{26}H_{38}O_{9}$ in Digitsaure $C_{26}H_{38}O_{10}$ noch ein tertiar gebundenes Wasserstoffatom zu Hydroxyl oxydiert worden sein.

Wir erteilen also der Saure $C_{22}H_{31}O_{10}N$ die formel V und erklaren uns die Bildung des Oxydationsproduktes $C_{22}H_{30}O_{10}$ (VI) bei der Einwirkung von Permanganat so, dass der Salpetersaureester des Lactols zum Lacton oxydiert wird und dass der carboxylhaltige Ring genau so aufgespalten wird wie beim Ubergang der Digitosaure (II) in Oxydigitogensaure (VII).



(V) *Saure* $C_{22}H_{31}O_{10}N$

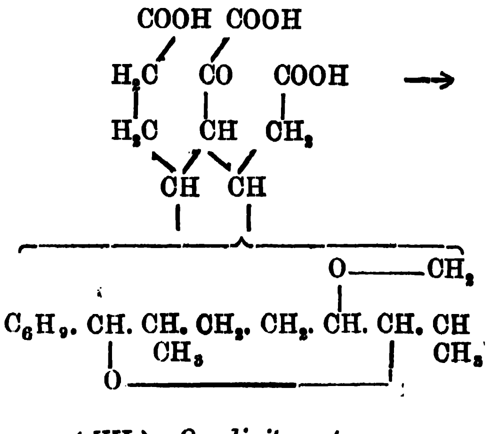


(VI) *Saure* $C_{22}H_{30}O_{10}$

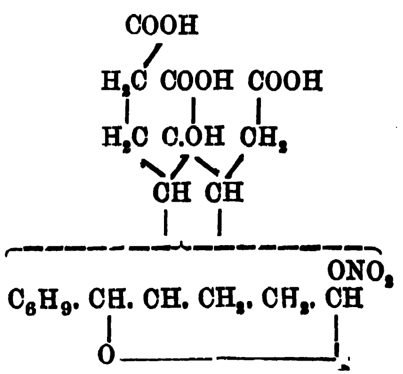
(II) Einwirkung von Salpetersaure auf Oxydigitogensaure.

Bei der Oxydation der Oxydigitogensaure (VII) mit Salpetersaure entsteht eine krystallisierte Saure $C_{21}H_{21}O_{11}N$ (VIII); sie ist dreibasisch und liefert einen krystallisierten Trimethylester (IX); beim Erwarmen mit Kalilauge spaltet sie salpetrige Saure und vielleicht Salpetersaure ab und geht in ein harzartiges Produkt uber; beim Erhitzen des Trimethylesters $C_{24}H_{37}O_{11}N$ im Hochvakuum spaltet er salpetrige Saure ab und gibt einen krystallisierten Ester $C_{24}H_{36}O_{9}$ (X), der bei der Verseifung eine Tricarbonsaure $C_{21}H_{30}O_{9}$ liefert. Diese Saure enthalt, wie die Titration beweist, ausser den 3 Carboxylgruppen 1 Lactongruppe und auch eine nach Zerewitinoffs Methodenachweisbare Hydroxylgruppe.

Eine Deutung fur den Reaktionsverlauf versuchen wir hier auf demselben Wege zu finden wie bei der Digitosaure. Nach den fruher angestellten Ermittlungen besitzt die Oxydigitogensaure (VII) wahrscheinlich die Formel einer α-Ketonsaure; bei der Behandlung mit Salpetersaure verliert sie nicht 4 Kohlenstoffatome wie Gitogensaure und Digitosaure, sondern 5. Wir nahmen an, dass 4 Kohlenstoffatome aus der Seitenkette stammen und eines auf der Gruppe. CO. COOH. Ferner wird auch hier ein tertiares Wasserstoffatom zu Hydroxyl oxydiert, so dass sich der Übergang der Oxydigitogensaure (VII) zur Saure $C_{21}H_{31}O_{11}N$ (VIII) folgendermassen darstellt :

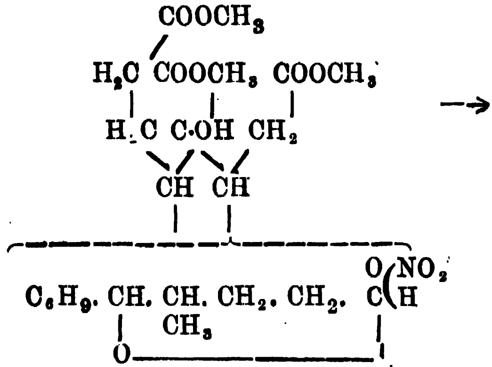


(VII) *Oxydigitogensaure.*

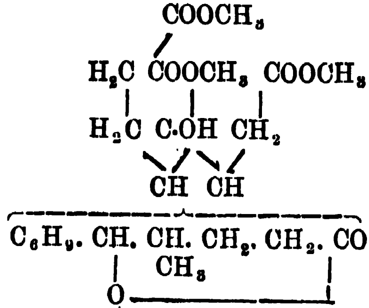


(VIII) *Saure* $C_{21}H_{31}O_{11}N$

Wir weisen auch hier nachdrucklich darauf hin, dass diese vorlaufige Deutung des Reaktionsverlaufes sicher verbesserungsbedurftig ist; immerhin gelingt es, auch das Verhalten des Trimethylesters $C_{24}H_{37}O_{11}N$ (IX), der bei der Destillation salpetrige Saur verliert und einen Ester $C_{24}H_{36}$-O_9 (X) entstehen lasst, durch diese Formulierung zu veranschaulichen :



(IX)



(X)

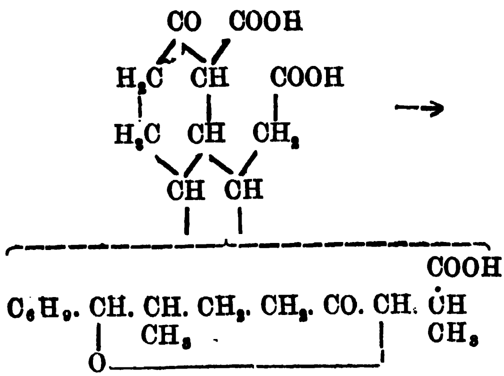
(III) Oxydation der Digitogensaure mit kalter Chromsaurelosung.

Wie bereits in der Arbeit von Windaus und Willerding[2] mitgeteilt worden ist, entstehen bei der Oxydation der Digitogensaure mit heisser Chromsaurelosung 3 Sauren, eine Pentacarbonsaure $C_{26}H_{38}(_{36})O_{12}$, eine Tricarbonsaure C_{26}-$H_{36}O_9$ und α-Methyl-glutarsaure. Die Saure $C_{26}H_{36}O_9$. die

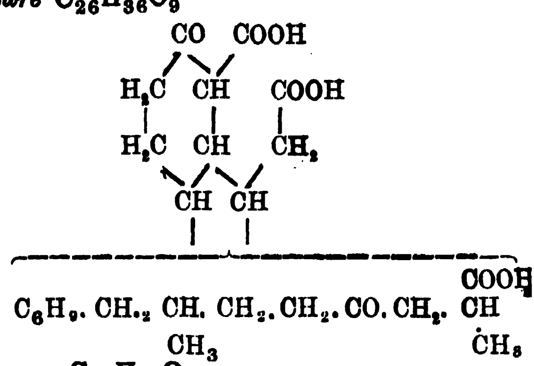
selbst nicht krystallisiert, wurde durch ihren schonen Trimethylester charakterisiert. Wir haben nun gefunden, dass diese Saure $C_{26}H_{36}O_9$ schon mit kalter Chromsaurelosung aus Digitogensaure gebildet wird. Wir glauben darum, dass der carbonylhaltige Ring der Digitogensaure unverandert geblieben ist. und dass die Seitenkette in der Saure $C_{26}H_{36}O_9$ (XI) angegriffen ist.

Um die Formel des Esters $C_{29}H_{42}O_9$ sicherzustellen, haben wir ihn partiell verseift und haben einen einfach sauren Dimethylester und einen zweifach sauren Monomethylester erhalten; dann haben wir den Ester $C_{29}H_{42}O_9$ mit Eisessig und Jodwasserstoffsaure behandelt und sind uber ein jodhaltiges Zwischenprodukt zu einer Tricarbonsaure $C_{26}H_{38}O_8$ (XII) gekommen, in der augenscheinlich der Oxydring aufgespalten und reduziert ist.

Der weitere Abbau der hier beschriebenen Stoffe wurde sicher neue Einblicke in die Konstitution des Digitogenins gestatten; leider wird die Fortfuhrung der Versuche durch die Kostbarkeit des Materials sehr erschwert.



(XI) *Saure* $C_{26}H_{36}O_9$



(XII) *Saure* $C_{26}H_{38}O_8$

I. Saure $C_{22}H_{31}O_{10}N$

1 Teil Digitosaure wird vorsichtig mit 5 Teilen rauchender Salpetersaure (1,5) ubergossen; die Reaktion ist ziemlich heftig, es wird ausser Stickoxyden auch Kohlendioxyd entwickelt und die Digitosaure geht in Losung. Man fallt nach dem Stehen uber Nacht das Oxydationsprodukt mit Wasser aus und krystallisiert es mehrmals aus siedendem Eisessig um. Die neue Saure ist fast unloslich in Wasser und Ather, ziemlich gut loslich in Eisessig und Alkohol. Beim Erhitzen im Schmelzpunktsrohrchen farbt sie sich bei 230° braun, bei 242° ist sie vollig zersetzt. Ausbeute 20%.

3,177 mg. Substanz gaben 6,571 mg. CO_2, 1,906 mg. H_2O.
4,328 mg. „ „ 0,111 ccm N (17° 757 mm).

$C_{22}H_{31}O_{10}N$	Ber. C 56,29%	H 6,61%	N 2,98%
	Gef. „ 56,40	„ 6,56	„ 3,01

Titration: 6,763 mg. Substanz verbrauchten 0,29 ccm n/10-Lauge.

Aquivalentgewicht: $C_{22}H_{31}O_{10}N$ (zweibasisch) Ber. 234 Gef. 233.

Wird die Saure $C_{22}H_{31}O_{10}N$ in der ublichen Weise mit atherischer Diazomethanlosung behandelt, liefert sie einen schon krystallisierten Dimethylester, der nach dem Umkristallisieren aus Methylalkohol bei 194 – 195° unter Zersetzung schmilzt. Der Ester ist loslich in Alkohol, fast unloslich in Ather, er krystallisiert in feinen Nadeln.

2,963 mg Substanz gaben 6,307 mg. CO_2, 1,835 mg. H_2O.
3,404 mg „ „ 3,212 mg AgJ.

$C_{24}H_{35}O_{10}N$	Ber. C 57,95%	H 7,04%	OCH_3 12,47%
	Gef. „ 58,05	„ 6,88	„ 12,46

Beim Erwarmen des Esters mit methylalkoholischer Kalilauge wurden 3 Aquivalente Alkalilauge verbraucht; in der Verseifungsflussigkeit liess sich salpetrigsaures Salz nachweisen.

Oxydation : 1 Teil Saure $C_{22}H_{31}O_{10}N$ wurde in 100 Teilen n/5-Natronlauge gelost und so lange mit 2%iger Kalium permanganatlosung behandelt, bis die Farbe des Permanganats etwa $\frac{1}{2}$ Stunde bestehen blieb. Nach beendigter Reaktion wurde das Gemisch mit schwefliger Saure und Schwefelsaure versetzt und 10 mal mit Essigester ausgeschuttelt; der Essigesterextrakt wurde eingedampft und der Ruckstand aus Wasser umkrystallisiert.

Das neue Oxydationsprodukt ist in Wasser und den meisten organischen Losungsmitteln ausser Petrolather leicht loslich, es schmilzt zunachst bei 113°, erstarrt dann wieder und schmilzt nunmehr erst bei 172°.

3,057 mg Substanz (bei 100° getrocknet) gaben 6,239 mg CO_2, 1,909 mg H_2O.

3,520 mg Substanz („ „ „) „ 7,159 mg CO_2, 2,126 mg H_2O.

$C_{22}H_{30}O_{10} \cdot H_2O$ (?) Ber. C 55,93% H 6,78%
Gef. „ 55,68 55,50 „ 6,99 6,76

Titration : 8,054 mg Substanz verbrauchten in der Kalte 0,51 ccm n/10-Lauge.

Aquivalentgewicht : $C_{22}H_{30}O_{10} \cdot H_2O$ (?) (dreibasisch)
Ber. 151 Gef. 157.

3,117 mg Substanz (bei 135° getrocknet) gaben 6,575 mg CO_2, 1,994 mg H_2O.

$C_{22}H_{30}O_{10}$ (?) Ber. C 58,14% H 6,61%
Gef. „ 57,56 „ 7,16

II. *Saure* $C_{21}H_{31}O_{11}N$.

1 Teil Oxydigitogensaure wird vorsichting mit 5 Teilen rauchender Salpetersaure 1,52 ubergossen; unter heftiger Reaktion, bei welcher reichlich Kohlendioxyd entwickelt wird, geht die Oxydigitogensaure in Losung. Nachdem die Hauptreaktion voruber ist, erhitzt man die salpetersaure Losung auf dem Wasserbad, bis die Gasentwickling aufhort. Hierzu sind etwa 2 Stunden erforderlich, dann wird die Losung bis zur Trubung mit Wasser versetzt, worauf sich im

Laufe einiger Stunden die Hauptmenge (25%) des Oxydationsproduktes in schonen Nadeln abscheidet; aus den Mutterlaugen fallt im Laufe einiger Tage noch eine weitere Menge (5%) aus.

Aus Eisesing umkrystallisiert bildet die neue Saure glanzende Blattchen und schmilzt bei 218 - 220° unter Zersetzung; sie ist leicht loslich in Alkohol und Eisessig, schwer loslich in Ather und in Wasser.

3,687 mg Substanz gaben 0,095 ccm N (21°, 751 mm).
2,97 mg „ „ 5,772 mg CO_2, 1,688 mg H_2O.

$C_{21}H_{31}O_{11}N$	Ber.	C 53,28%	H 6,55%	N 2,96%
	Gef.	„ 53,02	„ 6,36	„ 2,96

Titration : 0,0463g Substanz verbrauchten 2,75 ccm n/10-Lauge.

Aquivalentgewicht : $C_{21}H_{31}O_{11}N$ (dreibasisch Ber. 158. Gef. 165.).

Beim Erwarmen mit alkoholischer Kalilauge spaltet die Saure salpetrige. Saure ab und verbraucht genau 4 Aquivalente Alkalilauge.

Der mit atherischer Diazomethanlosung bereitete Trimethylester krystallisiert in Nadeln vom Schmelzp. 171°, er ist leich loslich in Alkohol, sehr schwer loslich in Ather.

3,017 mg Substanz gaben 6,191 mg CO_2, 1,868 mg H_2O.
2,981 mg „ „ 6,102 mg CO_2, 1,809 mg H_2O.
3,578 mg „ „ 0,087 ccm N (19°, 744mm).
2,674 mg „ „ 3,639 mg AgJ.
3,094 mg „ „ 4,141 mg AgJ.

$C_{24}H_{37}O_{11}N$

Ber.	C 55,92%	H 7,18%	N 2,72%	OCH_3 18,06%
Gef.	„ 55,99 55,85	H 6,83 6,79	N 2,78	„ 17,99 17,70

Molekulargewichtsbestimmungen :

0.313 mg	Substanz,	4,108 mg Campher,	Erniedr.	6°,	Mol.-Gew. 508
0,497 mg	„	4,918 mg „	„	9°	„ 449
0,298 mg	„	2, 82 mg „	„	8,5°	„ 497
0,215 mg	„	2, 49 mg „	„	6,5°	„ 532
0.418 mg	„	7, 56 mg „	„	4,5°	„ 492
0,228 mg	„	3, 76 mg „	„	5,0°	„ 485

$C_{24}H_{37}O_{11}$ Mol.-Gew- Ber. 515 Gef. 494.

Destillation des Esters im Hochvakuum : Der Ester $C_{24}H_{37}O_{11}N$ wurde aus einer kleinen Retorte im Hochvakuum uberdestilliert und ging bei einer Temperatur des Luftbades von etwa 250° als braunes Ol uber. Das erhaltene Destillat wurde mehrmals aus Methylalkohol umkrystallisiert und dadurch von hartnackig anhaftenden braunen Verunreinigungen befreit; In den schwerer loslichen Fraktionen stecken sehr kleine Mengen von Verbindungen, die bei 176° und 157° schmelzen, der Hauptteil des Destillats (50%) schmilzt konstant bei 142°, er krystallisiert in derben Nadeln und ist leicht loslich in Alkohol, schwer loslich in Ather und Amylather; die Probe auf Stickstoff ist negativ.

2,87 mg Substanz gaben 6,366 mg CO_2, 1,86 mg H_2O.
3,25 mg „ „ 4,654 mg AgJ.
4,153 mg „ „ 5,952 AgJ.
$C_{24}H_{36}O_9$ Ber. C 61,53% H 7,69% OCH_3 19,87%
Gef. „ 61,45 „ 7,31 „ 18,95 18,92

Der mit methylalkoholischer Kalilauge verseifte Ester gab eine Saure, die aus Ather in feinen Nadeln vom Schmelzpunkt 215-216° krystallisierte; sie ist sehr leicht loslich in Alkohol, schwer loslich in Ather.

3,295 mg Substanz gaben 7,117 mg CO_2, 2,013 mg. H_2O
3,145 mg „ „ 6,775 mg CO_2, 1,930 mg H_2O.
$C_{21}H_{30}O_9$ Ber. C 59,13% H 7,03%
Gef. „ 58,93 58,76 „ 6,83 6,81

3,85 mg Substanz verbrauchten 0,265 ccm N/10-Lauge.
0,0571 mg „ „ 3, 67 ccm N/10-Lauge,

Aquivalentgewicht : $C_{21}H_{30}O_9$ (dreibasisch).

Ber. 142 Gef. 144 156

In der Hitze wurde mehr Alkalilauge Verbraucht.

0,0571 g Substanz verbrauchten 4,52 ccm n/10-Lauge.

III. *Verseifung des Esters* $C_{29}H_{42}O_9$.

(Nach Versuchen von O. Linsert).

Der Ester $C_{29}H_{42}O_9$ lasst sich aus den Mutterlaugen, die, bei der Darstellung der Digitogensaure abfallen, in einer Ausbeute von etwa 10% isolieren und mit dem fruher beschriebenen Ester[3] durch Analyse und Mischschmelzpunkt identifizieren.

3,098 mg Substanz gaben 7,426 mg CO_2, 2,303 mg H_2O.
4,076 mg „ „ 5,575 mg AgJ.

$C_{29}H_{42}O_9$	Ber.	C 65,15%	H 7,92%	OCH_3 17,42%
	Gef.	„ 65,41	„ 8,32	„ 18,07

1 Teil Ester wurde in einer Mischung von 15 Teilen Eisessig und 10 Teilen 10% iger Schwefelsaure gelost und das Gemisch 1 Stunde am Ruckflusskuhler gekocht Die noch heisse Losung wurde mit Wasser bis zur Trubung versetzt; nach kurzer Zeit begann das Verseifungsprodukt auszukrystallisieren. Das Rohprodukt wurde in der ublichen Weise in einen neutralen und sauren Anteil zerlegt; der saure Anteil wurde aus verdunntem Aceton umkrystallisiert und lieferte dabei den in derben Nadeln krystallisierenden sauren Dimethylester, der bei 125° schmolz. Ausbeute etwa 25%. In den Mutterlaugen fand sich der Monomethylester.

3,415 mg Substanz gaben 7,801 mg CO_2, 2,282 mg H_2O.
5,014 mg „ „ 4,289 mg AgJ.

$C_{28}H_{40}O_9 \cdot H_2O$	Ber.	C 62,13%	H 7,86%	OCH_3 11,52%
	Gef.	„ 62,32	„ 7,48	„ 11,31

Titration : 0,2707 g Substanz verbrauchten 5,41 ccm n/10-Lauge.

0,1225 g „ „ 2,41 ccm n/10-Lauge.

0,2333 g „ „ 4,50 ccm n/10-Lauge.

Aquivalentgewicht $C_{28}H_{40}O_9 \cdot H_2O$ (einbasisch).
Ber. 536 Gef. 500 508 518

Zur Darstellung des Sauren Monomethylesters lost man 1 Teil Neutralester $C_{29}H_{42}O_9$ in 10 Teilen Eisessig, fugt 10 Teile 20% iger Salzsaure hinzu und kocht 5 Stunden am Ruckflusskuhler. Das Verseifungsprodukt wird durch vorsichtige Wasserzusatz ausgefallt und aus Aceton umkrystallisiert. Der saure Monomethylester krystallisiert in feinen Nadeln, die bei 201° schmelzen.

5,351 mg Substanz gaben 2,463 mg AgJ.

$C_{26}H_{35}O_8$ $(OCH_3) \cdot H_2O$ Ber. OCH_3 5,90% Gef. OCH_3 6,08%

0,1129 g Substanz verbrauchten 4,35 ccm n/10-Lauge.
0,1160 g „ „ 4,57 ccm n/10-Lauge.
0,1257 g „ „ 4,81 ccm n/10-Lauge.

Aquivalentgewicht : $C_{27}H_{38}O_9 \cdot H_2O$ (einbasisch)
Ber. 262 Gef. 260 254 261

Saure $C_{26}H_{38}O_8$: 1 Teil Ester wurde mit 10 Teilen Eisessig und 6 Teilen Jodwasserstoffsaure (2,0) 3 Stunden am Ruckflusskuhler gekocht; nach dieser Zeit fallte man das Reaktionsprodukt durch Wasserzusatz aus; es ist eine methoxylfreie, aber jodhaltige Saure, die sich aus verdunntem Methylalkohol umkrystallisieren lasst. Beim Erhitzen im Schmelzpunktrohrchen zersetzt sie sich bei 240—250°; sie scheint nicht ganz einheitlich zu sein und enthalt etwas mehr Kohlenstoff und weniger Jod als der Formel $C_{26}H_{37}O_8J$ entspricht.

3,063 mg Substanz gaben 5,950 mg CO_2, 1,81 mg H_2O.
3,207 mg „ „ 6,252 mg CO_2, 1,883 mg H_2O.
3,719 mg „ „ 0,752 AgJ.

$C_{26}H_{37}O_8J$ Ber. C 51,65% H 6,10% J 21,0%
Gef. „ 53,12 53,30 „ 20,2
H 6,63 6,58

6,678 mg Substanz verbrauchten 0,351 ccm n/10-Lauge,
Aquivalentgewicht : $C_{26}H_{37}O_8J$ (dreibasisch)
Ber. 201 Gef. 190,

Der mittels Diazomethan bereitete Trimethylester ist dimorph, er zeigt den Schmlzp. 122° und 105°.

3,018 mg Substanz (122°) gaben 6,037 mg CO_2, 1,890 mg H_2O.
3,060 „ „ „ „ 5,998 „ CO_2, 1,847 „ H_2O.
3,947 „ „ „ „ 0,786 „ J.
4,462 „ „ „ „ 5,075 „ AgJ.
3,099 „ „ (105°) „ 6,20 „ CO_2, 1,99 mg H_2O.
2,837 „ „ „ „ 5,685 mg CO_2, 1,783 mg H_2O.

$C_{29}H_{43}O_8J$ Ber. C 53,87% H 6,66% J 19,66 OCH_3 14,4
Gef. „ 54,58 54,55 „ 7,01 6,89 „ 19,91 „ 15,03
„ 54,59 54,66 „ 7,23 6,98

Um aus der Saure $C_{26}H_{37}O_8J$ das Jod herauszunehmen, kochten wir die essigsauro Losung 2 Stunden mit Zinkstaub am Ruckflusskuhler; das Reaktionsprodukt wurde mit Wasser ausgefallt und aus verdunnter Essigsaure umkrystallisiert; die neue Saure ist jodfrei, sie schmilzt bei 273—274°.

3,004 mg Substanz gaben 7.210 mg CO_2, 2,214 mg H_2O.
2,814 mg „ „ 6,737 mg CO_2, 2,096 mg H_2O.

$C_{26}H_{38}O_8$ Ber. C 65,27% H 7,95%.
Gef. „ 65,48 65,33 „ 8,25 8,34

Titration : 6,200 mg Substanz verbrauchten 0,375ccm n/10-Lauge.
6,503 mg „ „ 0,353ccm n/10-Lauge.

Aquivalentgewicht : $C_{26}H_{38}O_8$ (dreibasisch)
Ber. 159 Gef. 165 163.

Der in der ublichen Weise bereitete Methylester schmilzt bei 125-126°.

2,881 mg Substanz gaben 7.101 mg CO_2, 2,319 mg H_2O.
4,693 mg „ „ 6,285 mg AgJ.

$C_{29}H_{44}O_8$ Ber. C 66,92% H 8,46% OCH_3 17,88%
Gef. „ 67,20 „ 8,94 „ 17,87.

References

1. Kiliani und Merk. Chem. Ber. Bd. 34, S. 3565 (1901).
2. Diese Zs. Bd. 143, S. 37 (1925).
3. Diese Zs. Bd. 143, S. 44 (1925).

(Hoppe Seyler's Zeitschrift fur Physiologische Chemie, 151, 86-97, 1926).

XXXIX Interaction of Phenylhydrazine with the Halogen derivatives of the substituted amides of Malonic acid.

by

R. K. Trivedi and C. M. Mehta.

In order to study the labile nature of the Chlorine atoms substituting the hydrogens in the reactive methylene group $-CH_2-$, the interaction of Phenylhydrazine with the compounds mentioned below was investigated.

(1) Dichloromalon-di-phenylamide.
(2) Dichloromalon-di-o-tolylamide.
(3) Dichloromalon-di-p-tolylamide.
(4) Dichloromalon-di-1:3:4 xylidide.
(5) Dichloromalon-di-m-dichloro-tolylamide
(6) Dichloromalon-mono-chlorophenylamide.
(7) Dichloromalon-mono-p-tolylamide.
(8) Chloromethyl chloromalon-di-o-tolylamide.
(9) Chloromethyl chloromalon-di-p-tolylamide.

All the above compounds reacted with Phenylhydrazine yielding their respective hydrazon derivatives. The compounds (1), (2) (3) and (4) gave rise to the general type $C_6H_5NHN{:}C{:}(CONHR)_2$ according to the equation

$$3C_6H_5\ NHNH_2 + Cl_2{:}C{:}(CONHR)_2 \longrightarrow C_6H_5NC{:}C{:}\ (CONHR)_2 + 2C_6H_5NHNH_2HCl.$$

while compounds (5) and (6) reacted with Phenylhydrazine yielding the compounds in which the chlorines in the nucleun remained unaffected.

The compounds (8) and (9) reacted with Phenylhydrazine in a similar way giving a tri-membered ring.

$$3C_6C_5NCNC_2 + \begin{matrix} Cl\diagdown & \diagup CONHR \\ & C \\ ClC_2C\diagup & \diagdown CONHR \end{matrix} + C_6C_5NHN \begin{matrix} & \diagup CONHR \\ \triangledown & C \\ H_2C & \diagdown CONHR \end{matrix} + 2C_6H_5NHNH_2HCl.$$

All the above hydrazone compounds are found to be very stable and resist boiling with water and alcohol.

XL. The velocity of reduction of the chlorines substituting the hydrogens of the reactive methylene group $-CH_2-$ in the compounds of the type $Cl_2C\begin{smallmatrix}\diagup CONHR \\ \diagdown CONHR.\end{smallmatrix}$ where R is Phenyl, Tolyl etc. group.

by

R. K. Trivedi and C. M. Mehta.

The velocity of reduction of the chlorine atoms was studied by treating the following compounds by means of hydriodic acid -HI- generated through the action of HCl on KI. (Kurt Meyer, loc. cit.; J C. S. T. 1921, 119, 951, 305).

(1) Dichloromalon-di-phenylamide.
(2) Dichloromalon-di-p-tolylamide.
(3) Dichloromalon-di-m-dichlorotolylamide.
(4) Dichloromalon-di-o-tolylamide.
(5) Dichloromalon- 1:3:4 xylidide.
(6) Dichloromalon-di-β-dichloronaphthylamide.
(7) Dichloromalon-di-peptylamide.
(8) Dichloromalon-di-propylamide.
(9) Dichloromalon-di-benzylamide.
(10) Dichloromalon-monochlorophenylamide.
(11) Dichloromalon-mono-p-tolylamide.
(12) Chloromethyl chloromalon-di-phenylamide.
(13) Chloromethyl chloromalon-di-p-tolylamide.
(14) Chloromethyl Chloromalon-di-o-tolylamide.

The velocity of reduction of chlorines was represented by obtaining the curves by plotting the time of heating along the abscissa and the percentage reduced along the ordinatee. It was observed from the nature of the curves of the above compounds that the velocity of reduction goes on increasing in series from compound (1) to (5). This is attributed to the nature of the groups attaches to the carbonyl groups between which the $-CCl_2-$compex is situated as well as to the inser-

tion and the position of the methyl groups in the phenyl nucleus. In each case the velocity of reduction is considerably lowered when fifty percent of the total chlorine is reduced.

The curves of the compounds (7), (8) and (9) indicate that when the radicals attached to the carbonyl group carry aliphatic chain the velocity of reduction is increased. If the chain is shorter the velocity of reduction is decreased.

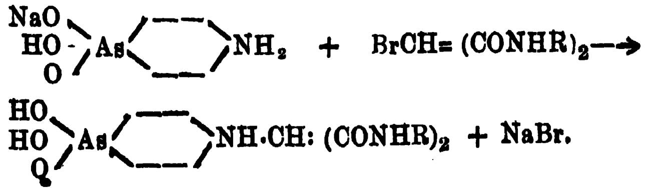
The compounds (10) & (11) show a drop in the velocity of reduction which is due to the presence of only one heavy radical in the complex.

The remarkable decrease in the velocity of the compounds (12), (13) and (14) is attributed to the presence of the $-ClCH_2-$grouping.

XLI A study of the interaction of Atoxyl (sodium p. aminophenyl arsonic acid) with the Halogen derivatives of the substituted amides of Malonic acid.

BY R. K. TRIVEDI AND C. M. MEHTA.

Herein it was proposed to study the reactivity of the chlorine atoms substituting the hydrogens of the reactive methylene group $-CH_2-$ with regard to Atoxyl but the reaction was not found to have taken place. This could be attributed to the comparative inactivity of the chlorine atoms towards atoxyl. On the other hand the Bromo derivatives of the substitutated amides of malonic acid interacted with atoxyl according to the following equation :—



This is due to the bromine atoms being comparatively more labile than the chlorine atoms similarly placed.

The following Compounds were selected to investigate the reaction:—

(1) Mono bromo malon-di-p-bromanilide.
(2) Mono bromo malon-di-p-tolylamide.
(3) Mono bromo malon-di-benzylamide.

The higher activity of bromine should be attributed to the higher atomic volume of bromine.

XLII The relation between the chemical activity and the absorption in the Ultra-violet of the compounds of the type

$$\begin{array}{c} Cl \\ Cl \end{array} \!\!>\! C \!<\!\! \begin{array}{c} CONHR \\ CONHR; \end{array} \quad \begin{array}{c} Cl \\ Cl \end{array} \!\!>\! C \!<\!\! \begin{array}{c} CONH_2 \\ CONHR \end{array} \quad \text{and} \quad \begin{array}{c} Cl \\ ClH_2C \end{array} \!\!>\! C \!<\!\! \begin{array}{c} CONHR \\ CONHR \end{array}$$

Where R is phenyl, tolyl etc. groups.

BY K. G. NAIK, Mme RAMART. R. K. TRIVEDI AND C M. MEHTA.

This study was undertaken with a view to throw some light on the relationship between the chemical activity of the chloro derivatives of the substituted amides of malonic acid and their absorption in the Ultra-violet.

The following compounds were selected for the study:—

(1) Dichloromalon-di-phenylamide.
(2) Dichloromalon-di-o-tolylamide.
(3) Dichloromalon-di-p-tolylamide.
(4) Dichloromalon-di-m-tolylamide dichloride.
(5) Dichloromalon-di-1:3:4 xylidide.
(6) Dichloromalon-di-heptylamide.
(7) Dichloromalon-di-benzylamide.
(8) Dichloromalon-mono-p-tolylamide.
(9) Dichloromalon-mono-chlorophenylamide.

(10) Chloromethyl chloromalon-di-phenylamide.
(11) Chloromethyl chloromalon-di-p-tolylamide.
(12) Chloromethyl chloromalon-di-p-tolylamide.

It can be seen here that the general absorption in compounds (2), (3) and (4) increases as we pass from ortho to para derivatives. The bands of absorption are shifted towards the visible region as follows.

Ortho ⟶ Meta ⟶ Para.

In the case of compounds (5) and (6) the curves are shifted more towards the visible.

In compounds (10), (11) and (12) the difference in the absorption is produced which is due to the absence of methylene group.

The results show that the more active is the molecule the higher is its absorption in Ultra-violet and the bands are shifted more towards the visible.

XLIII The velocity of Saponification of the chloro derivatives of the substituted amides of the malonic acid of the type

$$\begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CONHR \\ CONHR \end{matrix} \;:\; \begin{matrix} Cl \\ Cl \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CONH_2 \\ CONHR \end{matrix} \quad \text{and} \quad \begin{matrix} Cl \\ ClH_2C \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CONHR \\ CONHR \end{matrix}$$

Where R = Phenyl, Tolyl etc. groups.

BY K. G. NAIK, R. K. TRIVEDI AND C. M. MEHTA.

In order to investigate chemical activity of the chloro componnds as expressed by their velocity of saponification the following compounds were selected for study :—

(1) Dichloromalon-di-phenylamide.
(2) Dichloromalon-di-p-tolylamide.
(3) Dichloromalon-di-m-tolylamide dichloride,

(4) Dichloromalon-di-o-tolylamide.
(5) Dichloromalon-di-1:3:4 xylidide.
(6) Dichloromalon-di-heptylamide.
(7) Dichloromalon=di-propylamide.
(8) Dichloromalon mono-p-tolylamide.
(9) Dichloromalon monochlorophenylamide.
(10) Chloromethyl chloromalon-di-phenylamide.
(11) Chloromethyl chloromalon-di-p-tolylamide.
(12) Chloromethyl chloromalon-di-o-tolylamide.

The above compounds were made to react with standard alcoholic potash solution and titrated with standard hydrochloric acid at regular intervals. The results were tabulated in the form of curves representing the time as abscissa and the percentage of the compound saponified as ordinates.

In compounds (2), (3) and (4) the augmentation of the velocity of saponification proceeds as

ortho $\longrightarrow$ meta $\longrightarrow$ para.

The velocity of saponification depends upon the nature of the radical attached to the saponifiable imino -NH- grouping. It also depends upon the position of the methyl group with regard to the saponifiable imino group.

XLIV Formation of the sodium derivatives of compounds containing a reactive methylene ($-CH_2-$) group and study of the stability of the sodium atom with regard to the methylene group.

BY K. G. NAIK AND M. L. SHAH.

This work was undertaken to study the formation and the stability of the sodium compounds of the following substituted amides of malonic and methylmalonic acids and consequently the reactivity of the hydrogens of the methylene ($-CH_2-$) group in them:—

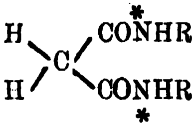
(1) Malon-di-phenylamide.
(2) Malon-di-p-tolylamide.
(3) Malon-di-m-tolylamide.
(4) Malon-di-o-tolylamide.
(5) Malon-di-1:4:5 xylidide.
(6) Malon-di- α-naphthylamide.
(7) Malon-di-β-naphthylamide.
(8) Malon-di-benzylamide.
(9) Malon-di-n-propylamide.
(10) Methylmalon-di-o-tolylamide.
(11) Methylmalon-di-p-tolylamide.

They all reacted with metallic molecular sodium yielding mono-sodium derivatives. In compounds (1) to (9), conversion of the group $-CH_2-$into $-CHNa-$ takes place; whereas in compounds (10) and (11), the conversion of group-$CH(CH_3)-$ into $-CNa(CH_3)-$ is effected.

(i) Malonamide (ii) Malon-mono-phenylamide and (iii) Malon-mono-o-tolylamide are found to remain unreacted.

Experimental results show that the above sodium derivatives formed are comparatively more stable than those of the amides of cyanacetic ester (Naik and Shah, J. Ind. Chem. Soc. 1931, 8, 45).

The velocity of the stability of the sodium atom in the above compounds is fully studied. When boiled with water, compounds (1) to (8) suffer slow decomposition, the velocity of hydrolysis varying with the groups attached to the nitrogen marked with an asterik in the following formula:—



The sodium derivatives of (10) and (11) are hydrolysed more rapidly than the above ones.

Chemistry Department,
The College, Baroda.

XLV On Active Charcoal.

BY M. D. AVASARE AND S. N. DAVE.

It has been known that the activity of charcoal, as measured by the magnitude of absorption, depends on its physical nature, the temperature and time of activation and on the nature of the gas in which it is activated. It has further been known that the magnitude of absorption on any given quality of active charcoal depends on the physical and chemical nature of the absorbate.

During a series of experiments undertaken to invostigate the corelation between the various factors that influence the activity of charcoal it is found that the magnitnde of absorption on the active Charcoal depends on the degree of evacuation to which the active charcoal is subjected previous to the study of absorption.

Under ordinary conditions of evacuation, absorption is increased owing to an increase on the pore diameter caused by a partial removal of the oxide film, but on intensive eva-

cuation its activity decreases to a large extent. The presence of the oxide film, therefore, appears to be essential for a high degree of activity.

Chemistry Department,
The College, Baroda.

XLVI. Formation and properties of Polyiodides.

BY M. D. AVASARE AND A. M. TRIVEDI.

Phase rule study of the system $NH_4I-I_2-CCl_4$ at 30°C showed the formation of a binary compound NH_4I_3 as confirmed by quantitative examination and by measurement of its dissociation pressure.

Treatment of an aqueous solution of ammonium iodide of definite concentration results in the formation of NH_4I_5– a very hygroscopic and unstable compound.

A detailed study of the solubility of iodine in aqueous solutions of (1) sodium, (2) potassium and (3) ammonium iodides has shown the formation of (a) NaI_3, KI_3 and NH_4I_3 only when the salt solutions of concentration range 0.017 M to 0.7 M were used and (b) the formation of NaI_5KI_5 and NH_4I_5 and NaI_7, KI_7 and NH_4I_7 when the sault concentration above 1 molar to saturation were employed.

XLVII Investigations on Hyponitritosulphates.

BY N. V. DHAKAN AND C. C. SHAH.

Pure potassium hyponitritosulphate has been successfully prepared and its chemical reactions have been studied. The following equations represent the course of its spontaneous decomposition:—

$$K_2SO_5N_2 = K_2SO_4 + N_2O \text{ ....(1)}$$
$$K_2SO_5N_2 = K_2SO_3 + 2NO \text{ ....(2)}$$

The course of the reaction has been found to depend on the concentration, temperature and the p_H value of the solution. In ordinary air, the solid salt decomposes, mainly, according to equation (1). Anhydrous carbon dioxide has no effect upon the salt. In saturated water vapour, the salt decomposes rapidly into sulphate and nitrous oxide. The aqueous solution of the salt is unstable and decomposes according to equation (1). All kinds of acids decompose the salt in the same way i. e. in accordance with equation (1),but alkalies appear to have a stabilising influence on the salt.

In acidic solution, potassium hyponitritosulphate is neither oxidised by commoner oxidising agents such as potassium permanganate, iodine, bromine, sodium bromate, hypoiodite, hypobromite etc., nor reduced by reducing agents such as stannous chloride and hydrochloric acid, stannous chloride and titanous chloride, sodium bisulphite and hydrochloric acid, zinc and acetic acid etc.

In alkaline solution, potassium permanganate and sodium hypochlorite oxidise it with the formation of potassium sulphate and nitric acid; all the nitrogen does not, however, get converted into nitric acid, some of it escapes as nitrous oxide

By the action of alkaline reducing agents a very small amount of ammonia is formed and a variety of products such as hydrazine, potassium sulphite, sulphate, etc., are detected in the reduction products.

The results obtained so far show that the hyponitritosulphuric acid, probably, exists in two forms:—

$$HO.SO_2.NO{:}N.OH \quad \ldots\ldots\ldots\ldots\ldots (1)$$
$$HSO_3,N.O\ N.OH \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Sodium and ammonium hyponitritosulphates and the doble salts of zinc, cobalt, manganese, cadmium, silver, and barium have been prepared and their chemical properties are being examined.

XLVIII Oxidation of Hydroxylamine sulphate and hydrochloride by means of potassium permanganate.

BY N. V DHAKAN AND C. C. SHAH.

In the reduction of nitric acid to ammonia, hyponitrous acid has been considered as an intermediate product (Jour. Phy. Chem. 1926, V. 30, P. 1222). But it has been shown by Partington and Shah (Jour. Chem. Soc. 1931 part I p. 2071), that hyponitrous acid cannot be reduced to ammonia though it can be oxidised to nitric acid to a certain extent. Leaving out nitrogen, hydroxylamine should be the first reduction product of hyponitrous acid. In order to elucidate this behaviour, experiments have been conducted to study the oxidation of hydroxylamine by potassium permanganate.

The course of the oxidation of hydroxylamine by potassium permanganate in neutral solution can be represented by the following equations :—

$$5(NH_2OH)_2H_2SO_4 + 4KMnO_4 = K_2SO_4 + 4MnSO_4 + 2KNO_2 + 2N_2O + 2\,N_2 + 20H_2O \qquad (1)$$

$$5NH_2OH{\cdot}HCl + 2KMnO_4 = KCl + 2MnCl_2 + KNO_2 + N_2O + N_2 + 10H_2O \qquad (2)$$

In acidic solution, the course of the oxidation is represented by the following equation :—

$$5(NH_2OH)_2H_2SO_4 + 10KMnO_4 + 10H_2SO_4 = 5K_2SO_4 + 10MnSO_4 + 8HNO_3 + N_2 + 26H_2O. \quad (3)$$

$$10NH_2OH{\cdot}HCl + 10KMnO_4 + 20HCl = 10KCl + 10\ MnCl_2 + 8HNO_3 + N_2 + 26H_2O \quad (4)$$

The course of the oxidation is dependent on the concentration and the p_H value of the solution. The temperature has little effect on the course of reaction.

It appears from the results so far obtained that the velocity of the oxidation reaction is very small. Further work is in progress.

XLIX Studies in Salting out effect.

BY M. D. AVASARE AND C. B. PATEL.

Salting out of non-electrolytes from aqueous solutions by electrolytes has been generally attributed to either (i) an increase in the internal pressure of the solvent caused by the added electrolyte or (ii) hydration of the electrolyte.

In this part of the investigation, it is attempted to study and classify the effects of different salts on the salting out of isoamyl alcohol, iso-butyl alcohol, aniline and O-toluidine in relation to the hydration capacity of these salts.

It has been found that though hydration does not seem to be the only cause for the salting out effect the magnitude of salting out effect generally runs parallel with the hydration capacity of the electrolyte. Further it has been observed that cations and anions. stand in the following order with respect to the magnitu of their salting out effectd.

$Na^{\cdot} > K^{\cdot} > NH^{\cdot}_4$ $SO_4'' >$ $Cl' > NO_3'$ — and that the same order is observed with respect to their capacity for hydration.

The following equation (Paul M. Gross, chem. rev; **62.** 92, 1933) has been found to hold good over the range 0·25 to 1·0 molar concentration of salt solutions employed in this investigation :—

$$v_a = k_1 C_s$$

where v_a is the additional volume in litres of solution which would be required to hold one molecule of a non-electrolyte in solution in presence of the added salt concentrations C_s in excess of the volume of water required for its solution in absence of the salt and k_1 is a constant.

Further, it has been observed that the salting out effects of electrolytes on the consecutive members of homologous non-electrolytes bear a constant ratio, given by the expression $\frac{s_1}{s_2} = k$, where s_1 and s_2 stand for the decrease in the solubility of the non-electrolytes in water caused by the addition of electrolytes.

L—Couleur et rèactivitè chimiqe dans la sèrie cinnamique; par Mme RAMART-LUCAS et M. R. TRIVÈDI.

(25-11-1932)

Si l'on considère plusieurs chromophores liés directement entre eux A, B, C, D......ils exercent une influence multuelle qui contribue de façon importante à déterminar leur état intérieur. Si l'on modifie l'un d'eux, A par exemple, en y introduisant un groupe T, non seulement A sera changé en A' mais ce changement aura une répercussion sur le ('couplage') de A et B en sorte que B n'aura plus le même état intérieur, ce qui aura pour conséquence une variation du couplage de B et C, etc. On peut prévoir, par suite, que l'introduction de T aura pour effet non seulement de changer A mais aussi de modifier l'état intérieur des autres chromophores B, C, D...et par suite leur réactivité chimique.

L'étude de l'absorption dans l'ultraviolet et de l'activité chimique des dérivés cinnamiques et méthylcinnamiques (acides, éthers, amides) confirment ce point de vue. L'introduction sur la chaine des dérivés cinnamiques d'un groupe CH^3 (qui par lui-même est incolore et n'a qu'une faible réactivité chimique), soit en $\propto$, soit en β, a pour effet de changer à la fois la couleur des dérivés cinnamiques et la réactivité des groupes acide, éther, amide. Les courbes d'absorption, des acides et des amides cinnamiques, $\propto$ et β méthylcinnamiques sont données. L'absorption générale décroit dans l'ordre suivant : dérivé cinnamique, $\propto$ méthylcinnamique, β méthylcinnamique.

Des mesures de vitesse d'éthérification ont été effectuées sur les acides; hydrocinnamique, cinnamique, $\propto$ méthyl, β méthyl, $\propto$, β-diméthylcinnamiques; ainsi que des mesures de vitesse d'hydrolyse des éthers et des amides correspondants. L'activité chimique du groupe fonctionnel décroît dans l'ordre: dérivés cinnamique, β méthylcinnamique, $\propto$ méthylcinoamique, $\propto$, β diméthylcinnamique,

Introduction.

L'un de nous a insisté (1) sur ce que le comportement chimique (énergies et vitesses de réaction) d'un chromophore introduit dans un carbure saturé doit changer en même temps que l'état interne de ce chromophore et par suite en même temps que la couleur introduite par ce chromophore; et sur ce que, quand cet état intérieur est le même (la couleur restant donc la même), les énergies de réaction du chromophore A sur un autre groupe B porté sur une autre molécule doivent être les mêmes; ainsi que probablement les vitesses de réaction (sauf gêne stérique apportée éventuellement par enroulement de la molécule dans le cas de très longues chaînes).

D'autre part, l'état intérieur d'un chromophore A dépend des atomes ou groupes d'atomes auxquels ils se trouvent liés. En sorte que dans une série homologue. les molécules H.A. CH^3.A, $CH^3.CH^2$.A auront un état intérieur différent et par suite une couleur et une réactivité différentes. Mais l'influence de l'allongement de la chaîne diminue rapidement, et dans une série homologue à chaîne normale, à partir du troisième terme, tous les termes supérieurs ont sensiblement une même couleur et, par suite, doivent avoir, même comportement chimique vis-à-vis d'un groupe B fixé sur une autre molécule. Il faut naturellement, comme il a été dit plus haut, envisager le cas où un enroulement de la molécule viendrait gêner l'approche de A et B.

Cette prévision s'est déjà trouvée vérifiée pour un grand nombre de séries homologues.

Par exemple les acides normaux $CH^3(CH^2)^nCOOH$ qui ont la même absorption depuis le terme pour lequel *n* est égal à deux, jusqu'à *n* égal à 14, (2) ont la même vitesse d'éthérifica-

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(1) Mme RAMART *C. R.*, **194**, p. 726 (1932).

(2) Mme RAMART, Mlle BIQUARD, M. GRUNFELD, *C. R*, 1930, t, **190**, p. 1196,

tion depuis l'acide butyrique jusqu'à l'acide stéarique (3). *Ajoutons que ces acides gras normaux ont sensiblement la même constante de dissociation depuis l'acide propionique.*

Il en est de même pour les amines primaires $CH^3(CH^2)n$ NH^2 qui depuis l'éthylamine out la même vitesse de réaction avec le bromure d'allyle (4). Or, M. Grunfeld (5) ayant mesuré l'absorption d'un certain nombre d'amines de cette série depuis la pentylamine jusqu'à la dodécylamine a trouvé conformément à ces prévisions que tous ces composés ont une absorption identique; il a dé plus trouvé, toujours dans le même ordre d'idées que ces amines ont les mêmes vitesses de réaction avec l'éther malonique.

On peut encore citer les travaux de Calvet (6) qui a constaté que les amides grasses à chaîne normale ont depuis la butylamide jusqu'à l'hexylamide les mêmes vitesses de réaction et les mêmes énergies de réaction. Or, Mme Ramart et Mme Grumez ont trouvè que ces amides qui avaient les mêmes réactivités avaient aussi la même absorption (7).

Enfin M, Ruzicka (8) en mesurant les vitesses avec lesquelles les cétones se combinent avec l'hydroxylamine, trouvé que la vitesse d'oximation est sensiblement la même pour les méthylcétones $CH^3.CO.(CH^2)nCH^3$ depuis la méthylpropylcétone jusqu'à la méthyltétradécylcétone. Or, d'après Rice (9) toutes ces cétones ont la même absorption depuis la propyl-

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(3) SUDBOROUGH et GITTINGS, *J. Chem. Soc.*, 1908, t. **93**, p. 210.

(4) MENTSCHUTKIN, *Ber. dtsch. Chem. Ges.*, 1897, t. **30**, p. 2775.

(5) GRUNFELD, *C. R.*, 1931, t. **192**, p. 1560.

(6) CALVET, *C. R.*, t. **192**, p. 1569 (1931).

(7) Mme RAMART et Mme GRUMER, *Bull. Soc. Chim.* 1932, t. **51**, p. 1538.

(8) RUZICKA et J. B. BUIJS, *Helv Chim, Acta*, t. **15**, p. 3 (1932).

(9) RICE, *Prod. Roy. Soc., London*, 1915, t. **91**, p. 65.

méthylcétone jusqu'à la nonylméthylcétone (il n'a pas étudié les termes supérieurs).

Plus généralement et en abrégé (10) :

" Lorsque dans diverses molécules, par ailleurs absolument quelconques, un chromophore introduit la même couleur cela signifie qu'il a même état intérieur, donc même réactivité chimique vis-à-vis d'un groupe B sur une molécule voisine".

Soit maintenant plusieurs chromophores A, B, C, D, liés directement entre eux, ils exercent une influence mutuelle qui contribue de façon très importante à déterminer leur état intèrieur. Si l'on modifie l'un d'eux : A par exemple, en y introduisant un groupe T (ainsi lorsque dans C^6H^5 on introduit un radical R pour former $R.C^6H^4$). Ce changement aura une répercussion sur le " couplage " de A (qui en fait sera devenu A' par suite de l'introduction de T) et B, en sorte que B n'aura plus le même état intérieur, ce qui aura pour conséquence une variation de " couplage " de B et C, etc.

On peut alors prévoir que la modification de A, par suite de l'introduction de T sur ce groupe, aura pour effet non seulement de changer ce dernier, mais aussi l'état intérieur des autres chromophores B, C, D et par suite, forcément, leur comportement chimique.

Considérons par exemple les acides arylacryliques :

Ar.CH=CH.COOH ou leurs dérivés éthers, amides, nitriles. D'après ce qui précède toute substitution dans l'un des chromophores doit modifier l'état interne, donc l'absorption et le comportement chimique des autres chromophores présents puisqu'ils lui sont liés directement et par suite s'influencent mutuellement.

Les faits observés par M. Ionescu dans l'étude de l'absorption des arylidènes-indanediones et leur activité chimique sont en accord avec ce point de vue.

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(10) Mme RAMART, *Bull. Soc., Chem.* [4], t. **51**, p. 329; 1932.

Ce savant sous la direction de M. Radulescu (11) prépare un certain nombre d'arylidènes-indanediones de formule générale

 où ($R=H, Cl, CH^3, OH, NH^2$)

Il mesure l'absorption de chacun de ces composés et il constate que le " front rouge " (expression employée par M. Radulescu pour désigner la partie du spectre la plus voisine du visible) est de plus en plus proche du visible à mesure que R représente H, Cl, CH^3, OH, NH^2.

Chacun de ces composés est ensuite condensé avec une molécule possédant un groupe méthylénique actif tel que l'acide malonique (la condensation s'effectue entre la fonction éthylénique et le groupe CH^2).

L'expérience montre que la facilité avec laquelle se fait cette condensation est variable avec la nature du radical R qui se trouve en para vis-à-vis de l'atome de carbone fixé sur l'un des atomes de carbone doublement lié. La vitesse de réaction diminue à mesure que R est successivement H, Cl, CH^3, OH, NH^2.

Ce savant ajoute que ces exemples sont d'autant plus intéressants que cette diminution de l'activité chimique est provoquée par la présence des groupes d'atomes éloignés de la partie de la molécule qui entre en réaction et que l'on ne peut par suite invoquer un empêchement stérique.

Nous montrerons dans ce qui va suivre que l'introduction d'un groupe CH^3 (qui par lui-même est incolore et ne possède qu'une faible réactivité chimique) soit en α soit en β sur la chaîne des dérivés cinnamiques (acide, éther, amide) a pour effet de changer à la fois la couleur de ces dérivés et la réactivité chimique des groupes fonctionnels : acide, éther, amide.

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(11) RADULESCU (*Bull. Soc. Sciences de Cluj* (Roumanie), t. **11**, p. 155-156 (1924) et. p. 280-298.

Les propriétés des acides cinnamiques et de leurs produits de substitution sur la chaîne ont depuis longtemps attiré l'attention des chercheurs et l'on connaît actuellement d'intéressantes relations entre la structure de quelques-uns de ces composés et certaines de leurs propriétés physiques et chimiques.

En ce qui regarde leur réactivité, ce sont surtout les vitesses d'éthérification, de saponification, de fixation d'halogènes que l'on connaît le mieux.

Sudborough et ses collaborateurs ont en particulier mesuré les vitesses d'éthérification par $CH^3.OH$ en présence de catalyseur (ClH) des acides cinnamiques, des acides α et β halogénés, α cyan et α-phénylcinnamiques (12).

Ils constatèrent que la présence d'une liaison éthylénique en α vis-à-vis du carboxyle diminue beaucoup l'activité (en ce qui concerne l'ethérification) que ce dernier possède dans l'acide saturé correspondant.

D'autre part, l'expérience leur montra que tous les dérivés de substitution de l'acide cinnamique ont une vitesse d'éthérification plus faible que celle de ce dernier et qu'enfin, pour les dérivés monosubstitutés, des deux isomères c'est le dérivé β pour lequel la vitesse d'éthérification est la plus élevée.

Pour expliquer cette diminution d'activité chimique plus élevée pour les dérivés α substitués, on a invoque l' " empechment stérique ".

Pourtant un ensemble de faits nous conduit à attribuer non pas à l'encombrement spatial des radicaux mais surtout à leur influence sur le groupe fonctionnel acide, l'inertie de ce dernier.

Si en effet le volume seul intervenait, l'activité du carboxyle devrait être d'autant plus faible que le volume du radical fixé en α est plus grand. Par suite, en considérant les groupes d'atomes : CN et C^6H^5, l'influence paralysante,

(12) Sudboroueg et Lloyd, *J. Chem. Soc.*, 1898, t. **74** p. 81.

de ces groupes sur l'activité du carboxyle devrait augmenter quand on passe de CN à C^6H^5. Or, il n'en est rien ainsi qu'en témoignent les mesures de vitesses d'éthérification effectuées p ar Sudborough et Lloyd et qui sont consignées dans le tableau suivant :

	0/0 de l'cide éthérifiné.
Acide cinnamique...........	99,12
∝ phénylcinnamique......	74,94
∝ cyancinnamique........	50,32

La vitesse d'éthérification fut étudiée en chauffant à 100° pendant une heure les acides avec CH^3OH absolu en utilisant ClH conmme catalyseur (30/0 de ClH dans 10 cm^3 d'alcool).

Les radicaux alcoyles fixés sur la chaîne des dérivés cinnamiques :

acides, éthers; amides exercent également comme nous le verrons plus loin une action paralysante sur l'activité du carboxyle.

Les mesures d'absorption nous ont permis d'autre part de mettre en évidence que cette action paralysante provient non pas de la protection du radical acide par les radicaux alcoyles, mais d'une action mutuelle que s'exerce entre ces différents groupement.

On sait en efet que les alcoyles sont incolores dans l'ultraviolet moyen, par suite s'ils n'avaient aucune action sur les groupes d'atomes au voisinage desquels ils se trouvent fixés, les acides alcoylcinnamiques devraient avoir la même couleur que l'acide cinnamique.

Or, il n'en est rien, et les acides, éthers amides cinnamiques n'ont pas la méme absorption que leurs dérivés méthylés sur la chaîn.

La modification de couleur provoquée par la présence des groupes CH^3 correspond donc à une action mutuelle de ces derniers et des groupes fonctionnels ce qui entraîne forcément une variation dans les propriétés chimiques.

Et ceci permet de comprendre que la présence d'un groue CH^3 même en position β modifie de façon très notable l'activité chimique du carboxyle. Il change en effet l'état intérieur du groupe $C^6H^5.CH{=}CH$ (le styrolène et l'α-methyl-styrolène ont des couleurs différentes) et par suite celui de la liaison éthylénique. Or, comme l'influence sur le carboxyle de cette liaison éthylénique est importante, ainsi qu'en témoigne l'étude comparative des vitesses de réaction des dérivés cinnamiques et hydrocinnamiques, à toute modification de l'état intérieur de la liaison éthylénique doit correspondre une variation dans l'activité chimique de la fonction acide (ou de ces dérivés).

En ce qui regarde l'influence sur la réactivité chimique de la substitution en position α deux effets se superposent : la modification de l'état intérieur du groupe $C^6H^5.CH{=}CH$ et l'action mutuelle de CH^3 et du groupe fontionnel acide, ces deux groupes étant fixès sur le même carbone.

Et cela explique, sans qu'il soit nécessaire de faire intervenir la notion d'empêchement stérique, l'action paralysante du groupe CH^3 soit plus importante lorsque ce dernier est en position α.

Vitesses de reaction.

En dehors des travaux déjà cités de Sudborough et de ses collaborateurs sur les vitesses d'éthérification des acides cinnamiques : halogénés, cyané, phènylè nous n'avons trouvé aucune recherche sur l'étude de la réactivite chimique des dérivé cinuamiques suivant la position la nature des radicaux alcoyles fixés sur la chaîne (14).

(14) Les expériences de M. Vavon concernant l'hydrogénation des acides méthyl et diméthylcinnamiques ont porté seulement sur la mesure de l'activiié de la liaison éthylénique. Vavon et Husson, *C. R.*, 1923, t. 76, p. 989.

Nous avons mesuré les vitesses d'éthérifications des acides: hydrocinnamique, cinnamique, α-mèthyl, β-méthylcinnamiques et α, β-dimethylcinnamique, les vitesses d'hydrolyse des éthers et des amides correspondants.

Nous avons pu constater, et ceci est en aecord avec les conclusions de Sudborough concernant les dérivés halogénés, que, d'une façon tout à fait générale si l'on compare l'activité *des fonctions acide*, *éther*, *amide* d'une part dans la série hydrocinnamique, et d'autre part dans la série cinnamique α-méthyl et α, β-diméthylcinnamique, ces produits se rangent comme suit dans l'ordre d'activité chimique décroissante :

Dérivés hydrocinnamiques$\rightarrow$cinnamiques$\rightarrow\beta$-méthylcinnamiques$\rightarrow$ α-méthylcinnamiques $\rightarrow$ α, β-diméthylcinnamiques.

L'activité chimique du groupe carboxyle, mesurée par les vitesses d'éthérification, est la plus nette et sans doute aussi là plus intéressante puisque cette éthérification a été effectuée en l'absence de catalyseur.

Sur la fig. I sont tracés les courbes qui indiquent en fonction du temps, la quantité d'acide éthérifié en chauffant à 100° une solution d'acide à la concentration de $n/100$ dans l'alcool absolu en tubes scellés.

En ce qui regarde l'hydrolyse des éthers et des amides, les résultats obtenus confirment ceux qui concernent les vitesses d'éthérification. Les différences de vitesses de réaction sont toutefois moins accentuées surtout en ce qui regarde les amides, mais il faut tenir compte de ce que cette hydrolyse a été faite en présence d'un catalyseur.

La figure II contient les cour bes tracées en portant en abscisses les durées de chauffage et en ordonnées la quantité 0/0 d'éther hydrolysé en chauffant ce dernier en tubes scellés avec une solution hydroalcoolique de ClH.

La comparaison des résultats obtenus dansles séries hydrocinnamiques et cinnamiques montre combien est importante l'influence de la liaison éthylénique sur les vitesses de réaction des groupes : COOH, $CO \cdot NH^2$, $CO^2 \cdot CH^2 \cdot CH^3$.

Mesures d'absorption.

Parmi les composés dont nous avons mesuré l'absorption seuls les acides : cinnamique (15), α-méthyl et $\alpha.\beta$-diméthylcinnamiques, (mesures qualitatives) (16) avaient déjà été étudiées de ce point de vue.

Des mesures quantitatives ont été effectuées sur l'acide cinnamique par V. Henri (17) et par Arends (18). Les résultats de nos mesures en ce qui regarde ce dernier acide, sont les mêmes que ceux qui ont été trouvés par ces savants.

Nous avons étudié l'absorption des substances suivantes :

Acide cinnamique $C^6H^5CH{=}CH.CO^2H$; acide α méthylcinnamique $C^6H^5CH{=}C{<}{}^{CO^2H}_{CH^3}$; acide β méthylcinnamique $C^6H^5.CH(CH^3){=}CH.CO^2H$; acide α cyancinnamique C^6H^5. $CH{=}C{<}{}^{CO^2H}_{CN}$; ainsi que les éthers et les amides correspondants.

Dans la fig. (III) sont tracées les courbes d'absorption des acides: cinnamique (1), α méthylcinnamique (2), β méthylcinnamique (3). Nous donnons également les courbes du styrolène et α méthylstyrolène afin de mettre en évidence d'une part l'influence du groupe carboxyle sur le radical

(15) E. C. C. Baly et K. Schaefer, *Proc. Chem. Soc.*, t. **24**, p. 207.—M. Stobbe Berl, *Ber. dtsch. chem. Ges.*, 1925, t, **58**. p. 2859; 1910, t. **43**, p. 504; 1911, t. **44**, p. 1289; et 1919, t. **52**, p. 1021. — Crymble, A. W. Stewart, R. Wright et W. Glendimung, J. *Chem. Soc. London*, t. **99**, p. 451.

(16) Ley et Rincke, *Ber. dtsch. chem. Ges.* 1923, p. 971.

(17) Etudes de photochimie, Gauthier-Villars, Paris 1919, p. 139.

(18) Arends, *Ber. dtsch. chem. Ges.*, 1931, t. **64**, p. 1936,

$C^6H^5CH{=}CH$ (en comparant l'acide cinnamique et le styrolène) et d'autre part la modification d'absorption produite sur le styrolène par la présence d'un groupe méthyle en position α.

L'absorption des éthers α et β-méthylcinnamiques est analogue à celle des acides. Nous ne donnons pas la courbe de ces composés qui sont liquides et dont nous ne pouvons, par suite, garantir la pureté.

Dans la figure IV nous donnons les courbes des amides : cinnamique (1), α-méthylcinnamique (2), β-méthylcinnamique (3).

Enfin dans la figure V se trouvent les courbes du nitrile cinnamique (1) de l'acide α cyancinnamique (2) et celle du cinnamate d'éthyle (3).

Nous avons constaté que l'introduction des groupes CH^3 qui pourtant sont par eux-mêmes incolores dans cette région du spectre, modifient la couleur des dérivés cinnamiques.

Si l'on compare la couleur des dérivés cinnamiques et celle des dérivés méthylcinnamiques correspondants, on observe que le maximum d'absorption de ces derniers est situé plus loin vers l'ultraviolet et possède une intensité plus faible que les dérivés non méthylés. La modification d'absorption est plus importante pour les dérivés β méthylés que pour les α méthylés.

L'absorption générale diminue donc quand on passe d'un dérivé cinnamique (acide, amide) au dérivé α méthylé et de celui-ci au dérivé β substitué.

L'introduction en α d'un groupe CN modifie fortement la position de la bande de l'acide cinnamique; or les nitriles $CH^3(CH^2)^nCN$ n'ont aucune bande d'absorption définie pour des longueurs d'onde plus grandes que 2400 A.

PARTIE EXPÉRIMENTALE.

Vitesse d'éthérification.—Afin d'éviter autant que possible toute action secondaire nous avons effectué l'éthérification des acides en absence de catalyseur.

La méthode générale adoptée pour la détermination de la vitesse d'éthérification de chacun des acides est la suivante :

On a dissous 0,01 molécule gramme d'acide pur (séché dans un dessiccateur pendant trois jours) dans 50 cm^3 d'alcool éthylique absolu fraîchement distillé sur du sodium; 5 cm^3 de cette solution fut titrée au moyen d'une solution de soude 0,094 *n* en prenant comme indicateur la phénolphtaléine. On connaissait ainsi l'acidité de la solution au temps zéro.

La sensibilité de la phénolphtaléine, comme indicateur pour ces expériences, fut examinée comme suit: une quantité connue de l'acide (correspondante à celle qui fut employée dans chaque expérience) fut dissoute dans l'alcool et cette solution titrée au moyen de soude 0,094 *n*. La différence entre la quantité d'acide calculée et celle qui fut trouvée etait de l'ordre de 0,075 0/0.

Pour chaque expérience 9 ampoules contenant 5 cm^3 de la solution d'acide furent scellées et mises dans un bain d'eau bouillante. Après chaque heure de chauffage une des ampoules était prélevée et refroidie dans un courant d'eau glacée. L'ampoule était ensuite brisée et le contenu titré avec une solution de soude 0,094 *n*.

Vitesse d'hydrolyse des éthers.—La méthode suivie pour déterminer la vitesse d'hydrolyse de chaque éther fut la suivante: 0,01 molécule gramme d'éther fut dissous dans 100 cm^3 d'une solution de ClH*n*/2 alcoolique; 5 cm^3 de cette solution furent immédiatement titrés au moyen de soude ce qui donnait l'acidité de la solution au temps zéro.

On introduisit ensuite 5 cm^3 de cette solution dans une série d'ampoules qui furent scellées, puis plongées dans un bain d'eau bouillante.

Après chaque 1/2 heure une des ampoules était prélevée du bain, refroidie dans de l'eau glacée; le contenu était

ensuite titré avec de la soude 0,094 *n* en prenant comme indicateur la phénolphtaléine.

Pour chaque substance deux séries de mesures ont été effectuées et les résultats ont très bien concordé,

Vitesse d'hydrolyse des amides.—La méthode utilisée pour mesurer la vitesse d'hydrolyse des acides est identique à celle qui a été décrite pour mesurer la vitesse d'hydrolyse des éthers.

On dissout 0,01 molécule g. d'amide dans 100 cm^3 d'une solution de $ClH n/2$ alcoolique; 5 cm^3 de cette solution furent titrès au moyen de soude en présence de rouge congo; l'acidité de la solution était ainsi connue au temps zero; 9 ampoules contenant chacune 5 cm^3 de cette solution étaient plongées dans un bain d'eau bouillante. Après chaque 1/2 heure une ampoule était prélevée, refroidie et l'acidité du mélange était titrée. Ici encore pour chaque substance deux séries de mesures ont été effectuées.

Préparation des dérivés cinnamiques.

Tous ces composés étaient déjà connus et certains d'entre eux avaient été obtenus par différentes méthodes.

Nous avons choisi parmi ces méthodes celles qui étaient susceptibles de nous donner des produits purs exempts de substances secondaires absorbantes.

Synthèse des acides cinnamiques.—Les acides cinnamiques et méthylcinnamiques ont été préparés par la méthode de Perkin (19); cette dernière consiste à traiter un aldéhyde aromatique par un sel de sodium en présence de l'anhydride de cet acide :

$$Ar.CHO + R.CH^2.CO^2Na \rightarrow Ar.CH{=}CH.CO^2Na$$

C'est ainsi que pour obtenir l'acide α-méthylcinnamique nous avons chauffé en tubes scellés pendant 6 heures à 180°

(19) Perkin, *J. Chem. Soc.*, 1877, t. **31**. p. 393.

un mélange de 20 g. d'aldéhyde benzoïque et de 30 g. d'anhydride propionique (tous deux fraichement distillés) avec 10 g. de propionate de sodium pulvérise et soigneusement desséché. On verse ensuite le mélange dans H^2O, puis on chasse par entraînement à la vapeur d'eau l'excès d'aldéhyde. Le résidu est ensuite neutralisé par CO^3Na^2, filtrè à chaud puis acidulé par ClH. Après avoir été traité par du noir animal très pur, l'acide est purifiè par des cristallisations répétées dans de l'alcool à 95°.

L'acide β méthylcinnamique a étè préparé par saponification de son éther dont nous traiterons plus loin de la synthèse.

L'acide α cyancinnamique a éte préparé par deux méthodes différentes : l'une d'elles préconisée par Fiquet (20) consiste à chauffer un mélange équimoléculaire d'aldéhyde benzoïque et d'acide cyanacétique à 120°. On arrête de chauffer quand le mélange entre en ébullition, on laisse refroidir, puis on traite le tout par de l'eau: on entraîne à la vapeur d'eau, pour éliminer l'excès d'aldéhyde benzoïque. L'acide est ensuite purifié comme il vient d'être dit pour les acides cinnamiques.

Ce composé a été également obtenu par saponification de son éther dont nous exposerons plus loin la synthèse. *Enfin l'acide hydrocinnamique* a été prèparè par la méthode classique qui consiste à traiter un halogénure par CNK et hydrolyser le nitrile obtenu.

Synthèse des éthers cinnamiques.—Le cinnamate d'éthyle a été préparé en utilisant la méthode suivante : 100 g. d'acide, 100 g. d'alcool absolu et 20 g. de SO^4H^2concentré (à 94 0/0) furent chauffés au bain-marie pendant 7 à 8 heures. On chasse ensuite l'alcool en excès, on ajoute de l'eau au résidu, on lave la solution éthérée avec CO^3Na^2, on la sèche sur du sulfate de sodium anhydre. Après le traitement Rabituel on distille l'éther sous pression rèduite C'est un liquide bouillant à 130-131° sous 15 mm.

∝-*Méthylcinnamate d'éthyle.*—Nous avons employé la méthode de Claisen (21) pour obtenir cet éther. On introduit dans un ballon 5 g. de sodium en fil, environ 100 g. de propionate d'éthyle et l'on verse goutte à goutte sur ce mélange 25 g. d'aldéhyde benzoïque; on laisse refroidir, on agite de temps en temps le mélange: puis ce dernier est refroidi versr — 14°, (mélange de glace et de ClH) puis abandonné pendant 24 heures à la température ordinaire. Après ce temps on ajoute 30 g. d'acide acétique cristallisable et de l'eau, on épuise avec de l'éther, on lave la solution èthèrée à l'eau puis avec une solution de CO^3Na^2, etc...

L'éther ainsi obtenu est très soigneusement fractionne. Le rendement en éther pur, distillant à 150° sous 15 mm., est de 25 g.

L'éther ∝ cyanocinnamique a été préparé par la même méthode en faisant agir des quantités équimoléculaires d'éther cyanacétique et d'aldéhyde benzoïque en présence de sodium métallique; la température ayant été maintenue au-dessous de 13°.

Les éthers β méthyl et ∝. β-diméthylcinnamiques ont été préparés par la méthode de Réformasky (22) qui consiste à faire agir Zn ou Mg sur un mélange d'éther ∝ halogéne et d'aldéhyde ou de cétone suivant le cas, et à déshydrater l'éther-sel alcool tertiaire ainsi obtenu, Ces réactions peuvent être, pour les éthers ∝ méthyl et ∝, β-diméthylcinnamiques, résumées par le schéma suivant:

$$C^6H^5.CO.CH^3 + Br.CH^2.COOC^2H^5 \rightarrow$$

$$C^6H^5C\begin{cases} CH^3 \\ \text{—CH}^2COOC^2H^5 \\ OH \end{cases} \rightarrow C^6H^5\overset{CH^3}{C}{=}CH.COOC^2H^5$$

$$C^6H^5.CO.CH^3 + CH^3.BrCH.COOC^2H^5 \rightarrow$$

$$C^6H^5.C\begin{cases} CH^3 \\ \text{—}\overset{CH^3}{CH}.COOC^2H^5 \\ OH \end{cases} \rightarrow C^6H^5.\overset{CH^3}{C}{=}\overset{CH^3}{C}.COOC^2H^5$$

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(20) FIQUET, *Bull. Soc. chim.* (3), t. **7**, p. 11; *Ann. Chim.* (6), t. **29**, p. 442.

(21) CLAISEN, *Ber. dtsch. chem. Ges.*, 1890, t. **23**, p. 978.

Synthèse des amides cinnamiques —De façon tout à fait générale nous avons préparé les amides par action de NH^3 sur les chlorures d'acides obtenus eux-mêmes par action de $SOCl^2$ (bien purifié) sur les acides.

Les amides ainsi obtenues à l'état déjà pur, ont été purifiées par cristallisations répétées dans de l'alcool.

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4° *S'erie, t.* 58, *p.* 178, 1933,

LI.—Absorption et Reactivite Chimique de Certaines Classes D' Amides.

BY Mme. RAMART. M. M. NAIK, ET TRIVEDI

Les recherches que nous allons exposer ont pour objet l' etude de la variation de l'absorption et de la réactivité chimique d'un certain nombre d'amides dérivées de l'adide malonique et de l'acide acètylacétique

R.NH.CO.CH^2.$CONH^2$, R.NH.CO.CH .CO.NH.R,
CH^3.CO.CH^2.CO NH.R, R.NH.CO.CH^2.CO^2.C^2H^5

R.N.CO.CH^2CO.N(R)(CH^3) (R = C^7H^{15}; C^6H^5; CH^3.C^6H^4 (o. m. p.),
CH^3
naphtyle $\propto$ et β.

Dans chacune de ces substances la fonction amide étant liée, soit par son carbone, soit par son azote à des radicaux différents, la réactivité chimique de cette fonction doit varier suivant la nature de radicaux presens.

Si en effet nous considérons une molécule R'.CH^2.CO.NH.-R, l'état intèrieur de chaque groupe d'atomes sera fixé par les atomes auxquels il s'attache en sorte qur toute variation dans la structure de R ou de R' provoquera un changement à la fois dans les propriétés de CH^2 et dans celles de la fonction amid Réciproquement toute variation dans la structure de CH^2 et de CO.NH doit retentir sur l'état intérieur de R et de R.

Dans ces composés, la réactivité chimique du groupe CH^2 vis à vis de certains réactifs tels que S^2.Cl^2, S.Cl^2, S^2O-Cl^2, SO^3 ClH, SO Cl^2 etc. a été longuemen étudiée par l'un de nous et ses collaborateurs. (1).

(1) NAIK *Journ. Chem. Soc.* 1921 p. 379-85 1921 119, p. 1231-1242 NAIK et AVASARE, *Journ. Chem. Soc.* 1922 121 p. 2592-2595. NAIK et JADHAV *Jour. Ind. Chem. Soc.* 1926 III, p. 260-272. NAIK et SHAH. *Journ. Ind. Chem. Soc.* 1927, 1V p. 11-21. BHAT. *Journ. Ind. Chem. Soc.* 1927, IV, p. 425. AMIN. *Journ. Ind. Chem. Soc.* 1928. V, p. 580. SHAH *Jonrn. Ind. Chem. Soc.* 1930 VII, p. III. NAIK et TRIVEDI. *Journ, Ind. Chem. Soc.* 1930, pp. 239,

Il a ainsi été constaté que amides maloniques, cyanacéti-ques, acétylacétiques, réagissent sur ces reactifs par le groupe méthylènique en donnant des complexes, et que ces réactions s'effectuent avec une facilité variable suivant la nature des radicaux lies au groupe méthylènique.

En particulier, l'étude du comportement chimique de ces amides vis-à-vis du tétrachlorure de sélénium a conduit aux résultats suivants : si l'on traite soit l'amide malonique, soit une amide monosubstituée $NH^2.CO.CH^2.CO.NH.R$ par $SeCl^4$, on n'observe pratiquement aucune réaction. Mais si l'on s'adresse à des amides disubstituées $R.NH.CO.CH^2.CO.NH.R$; on obtient des combinaisons séléniées de formule :

$$(R.NH.CO.)^2\,C = Se = Se = C\,(CO.NH.R)^2.$$

D'autre part, si l'on classe les amides étudiées par ordre d'activité croissante avec $SeCl^4$, l'ordre est le suivant :

$R.NH.CO.CH^2.CO.NH^2$, $R.NH.CO.CH^2.CO.NH.R$,

$R.NH.CO.CH^2.CO^2C^2H^5$; $CH^3.CO.CH^2CO.NH.R$.

De plus, lorsque R est un radical tolyle, l'activité de la molécule décroit quand on passe du dérivé ortho au dérivé méta et de celui-ci à l'isomère para.

En ce qui regarde le mécanisme de ces réactions la question ne semble pas éclaircie de savoir si les amides réagissent soit sous la forme amide vraie soit sous une forme tautomère,

Dans tautes, as etudes e'etait en quelque sorte la variation dactirté chimique du groupe CH^2 suivant la natures des radieaux fixé sur ce groupe qui était observeé.

Nous avons entrepris l'étude de la réactivité chimique de la fonction amide dans ces composés par la mesure de leur vitesse de saponification, et nous avons déterminé leur absorption dans l'ultra violet.

Nous avons constaté que la vitesse de saponification pour une même série d'amides $R'.CH^2.CO.NH.R$ (formule dans laquelle R' représente NH .CO, R''.NH.CO, CH^3.CO.,

$CO^2C^2H^5$) diminue quand on passe d'une amide pour laquelle R est un alcoyle, à celle pour laquelle R est un aryle.

D'autre part, *pour chacune de ces séries*, lorsque R est un radical tolyle, la vitesse de saponification décroit quand on passe du dérivé ortho au dérivé méta et de ce dernier à l'isomère para et quand R est un naphtyle la vitesse de reaction décroit quand on passe du α naphtyle a l'isomére β. (exactement comme en ce qui regarde l'action de $SeCl^4$ sur ces mêmes amides).

Or l'étude des vitesses de saponification d'acétamides de formules

$$CH^3.CO.NH.Ar \text{ et } CH^3.CO.N\begin{matrix}\diagup Ar\\ \diagdown CH^3\end{matrix}$$ (Ar représentant

les radicaux phényle, ortho et para tolyle) effectuée par l'une de nous avec M.lle WOHL, (1) a conduit à des résultats différents. D'après les mesures faites, la vitesse de saponification de ces anilides diminue quand on passe de l'acétoparatolylamide son isomère ortho, et ceci tant en ce qui regarde les amides monosubstituées qu en ce qui concerne les amides disubstituées.

Il reste donc à trouver les raisons pour lesquelles se manifeste une telle modification dans le comportement chimique de ces deux classes d'amides.

Des arguments d'ordre chimique, (2) (e) aussi que l'étude de l'absorption dans l'ultraviolet de certaines amides, ont conduit à adettre que, en solution ces substances se trouvent en équilibre sous les deux formes amide et iminoalcool :

$$R.C\begin{matrix}\diagup\!\!\diagup O\\ \diagdown NH^2\end{matrix} \rightleftarrows R.C\begin{matrix}\diagup OH\\ \diagdown\!\!\diagdown NH\end{matrix}$$

(1) Mme RAMART LUCAS et Mlle WOHL C. R. t. 196, p. 120, 1933.

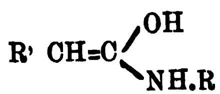
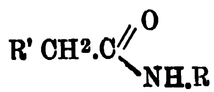
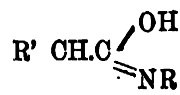
(2) TAFEL et ENOCH, *Ber. d. chem. Ges.*, 23, 1890, p. 104.
Mme RAMART LUCAS, Mlle Laclotre et Anagnostopoulos C. R. t. 185, p. 282, 1927. HANTZSCH *Ber. d. chem., Ges.*, 64 p. 661, 1931.

La proportion des formes en présence dépendant de la nature de R, du solvant et, selon la loi de Gibbs et Van t'Hoff, de la température.

On pouvait penser que la différence dans le comportement chimique des amides ici étudiées et dans celui des acét tolyl amides était dûeau fait que les solutions de ces deux classes d'amides contenaient des proportions différentes des deux formes : amide et iminoalcool.

Pourtant la fait que les acétatolylamides disubstituées, qui ne peuvent prendre la forme iminoalcool, se conduisent, (vis à vis des des alcalis) comme les acétolylamides mono-substituées, semble devoir écarter cette hypothèse.

Il parait possible d'expliquer la différence de propriétés des malon tolylamides et des acétolylamides, en admettant que les amides peuvent prendre, en solution, les trois formes tautomères' aminoalcool éthylénique (I); amide vraie (II', iminoalcool (III)

(I) (II) (III)

La proportion des formes on èquilibre varient naturellement suivant la constitution de R et de R' et aussi suivant la solvant.

Les amides maloniques, acétylacétiques possèdent un groupe méthylénique dont les atomes d'hydrogène sont particulièrement mobiles, ce qui doit faciliter l'apparition de la forme (I).

On sait d'autre part, que l'introduction dans l'acide ou l'amide benzoique d'un groupe CH^3 en ortho paralyse par

tiellement l'activité de la fonction amide ou acide; il est donc à penser que la diminution d'activité du groupe CONH dans les orthotolylamides, dérivées des acides malonique et acétylacétique, favorise également l'apparition de l'isomére (I). Cette hypothése semble d'autant plus raisonnable, que l'on admet actuellement que le malonate d'éthyle sodé possède la structure

$$\mathrm{CHO.CO.CH{=}C}\begin{array}{l}\nearrow \mathrm{OC^2H^5}\\ \searrow \mathrm{Na}\end{array}$$

En sorte que, si les amides peuvent prendre cette forme, on doit la rencontrer en proportion plus élevée dans les solutions d'orthotolyl malon imide et d'acétylacétortho-tolylamide.

Si la forme aminoalcool éthylénique réagit avec une vitesse plus grande que les autres formes avec les alcalis, on s'explique aisément que, pour les tolylamides ici étudiées, les dérivés ortho aient une vitesse de saponification plus grande que celle de leurs isomères méta et para, alors que c'est l'inverse qui se produit en ce qui regarde les acéto toluides pour lesquelles la forme (I) n'est guère à envisager, tout au moins en quantité appréciable. Les mesures d'absorption semblent bien confirmer les vues précédentes.

Aucune de ces substances n'avait encore à notre connaissance été étudiées du point de vue de l'absorption.

Nous avons constaté que les arylmalonamides $\mathrm{Ar.NH.CO.}$-$\mathrm{CH^2.CONH}$ et les malon diaryl amides $\mathrm{(Ar.NH.CO)^2{=}CH^2}$ ont des spectres tout à fait semblables, (compte tenu de la différence de constitution des radicaux Ar, et du fait que les corps de la première série ne contiennent qu'un groupe Ar.) Ceci indique que ces amides ont une même structure et que si elles existent en solution sous plusieurs formes en équilibre,

les proportions des formes en présence doivent, pour un radical Ar donné, être sensiblement les mêmes, pour les deux séries.

Nous avons d'autre part mesuré l'absorption d'une amide N disubstituée, la malon di (methylphényl) amide

$$\left(\begin{matrix} C^6H^5\diagdown \\ \quad\quad N\,CO \\ CH^3\diagup \end{matrix}\right)^2, C^2H^2$$

et nous avons constate qu'il existe une différence d'absorption très importante (comme dans le cas des acétanilides) entre une amide disubstituée comme la malondi (méthylphényl) amide, et une amide monosubstituée sur l'azote telle que la malondiphénylamide. Cette difference de couleur que il peut etre pestifiée par la presence du groupe CH^3 dans la malon di méthylphényl amide est telle (forme et position des bandes) qu'il faut admettre que les solutions de ces substances contiennent, tout au moins à l'état de milange des corps ayant des structures différentes.

Amide N disubstituée est beaucoup plus transparente que l'amide N monosubstituée; ses bandes se trouvent plus loin du visible et ont une intensité d'absorption beaucoup plus faible que celle de l'amide monosubstituée. (Voir fig. V).

Si la malon diphénylamide (et toutes les amides N monosubstituées qui ont été étudiées) peut d'aprés sa constitution prendre les trois formes: amide aminoalcool éthyléniquie, et iminoalcool, et par suite posséder l'un des groupe. I, II, III. la malondi (méthylphényl) amide ne peut avoir que les formes amide (I) et aminoalcool éthylènique (II) formes dans lequelles les atomes qui se trouvent fixés directement sur le radical aromatique ne sont liés que par une valence.

$$Ar.NH.\underset{\diagdown OH}{C}{=}CH \text{ (I) } Ar.NH.CO.CH^2 \text{(II) } Ar.N{=}\underset{\diagdown OH}{C}.CH^2 \text{ (III).}$$

Or d'après ce que l'on connait des relations entre la couleur et la structure des molécules organiques, les bandes

d'absorption de la forme iminoalcool (III) doivent se trouver plus près du visible et posséder une intensité d'absorption plus élevée que our les forme (I) ou (II).

On est insi conduit comme dans le cas des acétanilides à admettre que la forme iminoalcool est présente dans les solutions de malondiphénylamide (et dans toutes les amides monosubstituées) puisqu'elles ont des spectres qui correspondent à des structures semblables sans que l'on puisse toutefois en déterminer les proportions puisque l'on ne connait pas la couleur de cette forme à l'état pur.

D'autre part, si l on compare les spectres des solutions de l'acétanilide (fig. I courbe 2) à celui des solutions de la malonphénylamide (courbe 1), le spectre des solutions de l'acétoparatoluide (fig. II courbe 2) à celui des solutions de la malonparatolylamide (courbe 1), on n'observe, entre les duex amides dans mettre couple qu'une faible différence d'absorption ce qui correspond à une analogie de structure entre les acétanilides et les malonamides.

Si maintenant, on examine les courbes de l'acétorthotoluide, fig. II courbe 4, et de la malonorthotolylamide (courbe 3), on constate entre ces deux substances, une différence d'absorption notablement plus importante que dans les cas précédents. Il est par suite raisonnable de penser que ceste différence d'absorption correspond à la présence dans les solutions de malonorthotolylamide, d'une substance ayant une structure différente de celles que possèdent soit les acétanilides, soit les malonphényl ou malonparatolylamides.

En effet, pour un même radical Ar, les acétanilides $CH^3.CO.NH.Ar$ et les malonamides $NH^2.CO.CH^2.CO.NH\ Ar$ ne diffèrent du point de vue de leur constitution que par le fait que le CH^3 des-acétanilides se trouve dans les malonamides, remplacé par $NH^2.CO.CH^2$. Lorsque le radical aromatique Ar, est soi un phényle, soit un paratolyle, cette

différence dans la constitution se traduit par un faible différence d'absorption (ce qui est très compréhensible puisque l'absorption du groupe $NH^2.CO.CH^2$ doit être petite vis à vis de celle du reste de la molécule), alors que la différence d'absorption entre l'acétorthotoluide et la malonorthotolylamide est assez importante. Cette différence d'absorption doit donc être considérée comme correspondant à une différence dans la structure de ces deux amides ce qui confirme bien les conclusions auxquelles ont conduit les mesures de vitesse de saponification, à savoir que les différences entre le comportement optique et chimique des malontolylamides, d'une part, et celui des acétyloluides d'autre part, peuvent etre attribuées à la présence dans les solutions des malonamides de la forme aminoalcool éthylénique (III) qui pour les raisons énoncées plus haut existerait en quantité plus importante dans le cas des malonorthotolylamide.

(Reprinted from the " Bulletin de la Société Chimiqus de France " April 1934.

THE END.

I—On a Serious Difficulty in Cotter's Treatment of the Quantum theory.

By D. V. Gogate.

According to our present conceptions the thermal content of a monatomic solid is nothing more than the energy of the elastic vibrations about their positions of equilibrium of its atoms which are arranged in the form of a space lattice. If we apply the law of equipartition of energy to these vibrations we find that the mean kinetic energy of an atom is equal to its mean potential energy. In the kinetic theory of gases, assuming that the molecules of the gas are geometrical points endowed with mass exerting no force of attraction or repulsion on the neighbouring molecules, we obtain

$$\tfrac{1}{2}m\overline{c}^2 = \tfrac{3}{2} R_0 \theta$$

as value for the mean kinetic energy of a molecule of the gas. If this expression obtained for an ideal gas can also be taken to be its mean kinetic energy in the solid condition then the total mean energy in the solid condition of a molecule wuold be $3R_0$ and the atomic heat of a monatomic solid body at constant volume becomes

$$aC_v = \frac{a}{J}\,\frac{dE}{d\theta} = \frac{3R_0}{m_H J} = 5.96.$$

This is the law of Dulong and Petit according to which the atomic heat at constant volume of monatomic solid bodies has the value 5·96 independently of the temperature. This law however has been found to be true only for high temperatures, the lower the temperature the greater being the deviation from the law.

Now this variation of the specific heat with temperature has been accounted for by Debye by making use of Planck's Quantum Theory. The Quantum theory denies the equipartition of energy postulated by Maxwell, and gives a new law of partition of energy. Particular frequencies will be specially favoured by the solid and will therefore exist in greater strength. Since unit mass of the solid contains N atoms each

of three degrees of freedom it possesses 3N degrees of freedom, that is it is capable of vibrating in 3N different ways and these must be classified before we can apply Planck's law.

Cotter, adapting the treatment of Jeans and Lorentz effects this classification in the following manner :—

Let the unit mass of the solid under consideration be in the form of a rectangular parallelopiped whose linear dimensions are p, q and r. The vibrations will consist of trains of waves which will be reflected at the surfaces so that the angle of reflection is equal to the angle of incidence. If α, β, γ are the direction consines of any wave front then the waves after any reflection will travel in some one of the eight directions whose direction cosines are $\pm\alpha, \pm\beta; \pm\gamma$. In order that no energy may be gained or lost at the surface the distance travelled between any two successive reflections must be some multiple of $\lambda/2$ where λ is the wave length. In his treatment Cotter gives the relations

$$2\alpha p=\lambda x;\ 2\beta q=\lambda y;\ 2\gamma r=\lambda z$$

where x, y and z are integers, whence from the relations $\alpha^2+\beta^2+\gamma^2=1$ he deduces the equation

$$\frac{x^2}{p^2}+\frac{y^2}{q^2}+\frac{z^2}{r^2}=\frac{4}{\lambda^2}=\frac{4v^2}{V^2}. \qquad (1)$$

It should be noted that (1) is an equation of the 2nd degree.

But from an examination of the figure (See. L. U. Journal. 1925, p. 2) it is clear that if PQ be the path of a 'ray' travelling from the plane $z=0$ to $z=r$, and if α, β, γ be the direction cosines and l the length of PQ we have obviously

$$\frac{r}{l}=\gamma \qquad \text{and} \qquad l=z\frac{\lambda}{2}$$

where z is an integer,

$$\therefore\ 2r=\lambda z\gamma$$

Similarly we shall get

$$2p=\lambda x\alpha, \qquad \text{and} \qquad 2q=\lambda y\beta$$

for rays travelling between the other pairs of planes. Hence from the relation $\alpha^2+\beta^2+\gamma^2=1$ we deduce the equation

$$\frac{p^2}{x^2}+\frac{q^2}{y^2}+\frac{r^2}{z^2}=\frac{\lambda^2}{4} \qquad (2).$$

This is obviously an equation of the 6th degree.

If we substitute this equation in place of (1) in the treatment as given by Cotter the whole of the subsequent theory falls through.

As this result is utilized in accounting for the distribution of energy in the spectrum of a black body in accordance with the quantum theory the difficulty arising here makes that investigation also invalid.

"Scientific Bolshevism" is the name given to the Quantum Theory by the physical chemist Lewis. Explanation of the variation of the specific heat of solids with temperature and the energy distribution in the black body spectrum are two of the achievements of this theory. It appears however the claim to have explained these phenomena is anything but firmly established.

(Reprinted from L. U. Journal, 1925.)

II—A Note on Ultra-Short Waves and Radiation from Free Electrons.

By D. S. Kothari and D. V. Gogate.

Recently, Prof. Yagi[1] has described some experiments with a Magnetron. He has succeeded in producing waves of the order of 10 cms. and has given a semi-theoretical formula, $\lambda = 2ct$, where, c = velocity of light and t = time taken by the electron to move from the filament to the anode.

He has, however, given no theoretical discussion regarding the origin of his short waves and we are, therefore, giving a preliminary explanation. The work seems to be of great importance for it brings out several points of novel interest.

In the ordinary oscillatory circuits radiations are generated because of the oscillations of electric charge in a metallic conducting path consisting of an inductance and capacity. However, if an electron could be made to describe a closed path in space with frequency v, it should become a source of radiation of this frequency. It seems that in Prof. Yagi's experiments we have an almost direct proof that such radiations are taking place, though Yagi himself does not offer any such explanation.

The Magnetron is a diode valve with a cylindrical anode and an axial filament placed in a magnetic field acting along the axis of the cylinder. The field can be adjusted in strength. When the field is sufficiently increased most of the electrons will just fail to reach the anode as they move tangentially past its surface. Knowing this critical field

[1] Yagi. Proc. Inst. Radio Eng., Vol. 16, p. 715, 1928.

value and the anode voltage, e/m can be easily calculated.[1] At this critical field-value, in the anode cylinder there will be electrons moving in a closed path (almost circular of radius $b/2$), and therefore, radiating waves of wavelength.[2]

$$\gamma = 2.\ c.\ t. = 2c.\ \pi b \sqrt{\frac{2eV}{m}}$$

where V = anode voltage and b = radius of the anode. These waves are impressed on the oscillatory circuit of which the capacity is that between the anode cylinder and the filament. Oscillations are generated in this circuit and so the voltage of the anode undergoes slight fluctuations. But a slight increase in the anode-voltage above the critical value attracts most of the electrons that were previously moving only tangentially past it, whereas a slight decrease in the anode-voltage does not allow them to reach it. As in the critical condition the electrons are moving tangentially past the anode, a slight fluctuation in its voltage can attract them to it or repel them off from it. Thus the oscillatory current in the circuit, because of this reaction increases in strength.

There may seem one difficulty in this mode of explanation. From the filament electrons are issuing, and, they will be, while describing the closed path in the critical state, sources of approximately simple harmonic waves of constant amplitude but random phase. Lord Rayleigh's[3] analysis, however, of a large number of simple harmonic motions of constant amplitude and random phase clears this difficulty.

In order to verify the above theoretical considerations, we are attempting to repeat Yagi's experiments with a triode. As a preliminary, we have repeated the experiments of

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1 D. S. Kothari, Ind. Jour. Phy. p. 485, July, 1928. (The paper contains the description of a laboratory method of determining e/m with a triode valve. Yagi's arrangements are identical, though they were meant for another purpose. His curves are of the same form and they give as good values of e/m).

2 *Loc. cit* Yagi.

3 Lord Rayleigh's Sound. Vol. I

determining e/m and on short waves by B. Majumdar (*Ind. Jour. Phy.* 1928) Gill and Townsend (*Phil. Mag.* 1921) and others, and have found some interesting results.

It has been found that in the e/m experiments, the anode current which falls suddenly at the critical field value, shows a slight increase for smaller values of the field. This increase in the anode current is interesting. It seems to be an effect of the space-charge, for, the increase obtained is much less with increasing anode-voltage, or smaller filament current or when the grid is given a positive bias. Theory also indicates that an increase in the anode current for small values of the magnetic field is to be expected when space-charge is predominant.

We may also note that in the paper of Mr. B. Majumdar it is stated that the capacity of the anode and the grid as measured experimentally by Toshniwal's method [1] was found to be about 40 cms., whereas, if it is calculated from the wavelength of the short waves generated ($\lambda = 2.\pi\sqrt{CL}$), it comes out to be about 6 cms. only. This discrepancy is explained if the self-capacity of the wires forming the oscillatory circuit is taken into account. In calculating the frequency of the oscillations this self-capacity becomes a more predominating factor than the valve capacity.

Our best thanks are due to Prof. M. N. Saha for kind suggestions and continued guidance.

Physics Department.
Allahabad University.

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[1] G. R. Toshniwal, Jour. Sci. Inst., July, p. 220, 1928.

III—Effect of Direct Current on the Frequency of Sonometer Wire.

By D. V. GOGATE and Y. G. NAIK

The maintenance of oscillations of a sonometer wire by the passage of an alternating current through it has been studied in detail by Krishnaiyer and others (Phil. Mag., 1922, etc.). If, however, direct current of the value of about an ampere be passed through the wire, it is found that the frequency of the oscillations, for a fixed position of the two sonometer bridges, is slightly lower than what it is when no current is passing. This effect is best observed by tuning the sonometer with an electrically excited fork placed on the sonometer board. When the wire is tuned to this frequency it begins to vibrate with a large amplitude. These vibrations are observed with a low power microscope. If the the direct current be now passed through the wire, the amplitude of the vibrations is immediately reduced, and can be restored again to its original strength by shortening a little the length of the wire between the bridges.

We have verified that this lowering in frequency is not due to the heating effect of the current and is also not a magnetic effect. This effect can also be observed with an ordinary tuning fork and wires of any material.

The quantitative measurements and other interesting results will be published elsewhere.

Physics Laboratory,
Baroda College, Baroda.

(Reprinted from "Nature" May 31, 1930).

IV—Further Experiments on Ultra Short Waves.

BY D. V. GOGATE AND D. S. KOTHARI,

Abstract.

The experiments described in this paper are a continuation and extension of the experiments of Mr. B. Majumdar.[1] The effect of coupling two resonance circuits to the same value is also studied and from these measurements the interelectrode anode-grid capacity of the triode is determined. The effect of the self-capacity of the wires forming the inductance of the oscillatory circuit is also taken into account.

S. 1.

The oscillatory circuit used was like that of Gill and Townsend.[2] A French valve (Anode volts up to 600 V. Fil. Volts 5·5) similar to that used by Majumdar was used. The inductance of the oscillatory circuit was formed by two straight parallel bare eureka wires S. W. G. No. 16, separated by about a distance of 7 cms. from each other, the two ends at one extremity being connected to the anode and the grid pins of the valve (which was held inverted in a clamp) respectively and the other two ends bridged by a bye-pass condenser (0·003μF). The wave-length of the short waves generated was measured on a Lecher wire system coupled inductively to the oscillatory circuit, a R. F. milliammeter being used as the detector of the potential anti-nodes. The straight wires forming the inductance of the oscillatory circuit were gradually shortened in length, the wave-length of the oscillations being measured in each case. It was not found possible to reduce the length of the wires beyond a certain stage (23 cms. corresponding to $\lambda = 3$m.) as then the oscillations produced were too feeble to be detected, while for larger wavelengths a current of about 300 m A. was detected at the potential anti-nodes of the Lecher wires.

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[1] B. Majumdar, Ind. Jour. Phy., 1928.

[2] Gill and Townsend, Phil. Mag., 1921.

It was found that for small changes Δl in the length l of the inductance wires the wave-length changed by about $4\Delta l$, *i. e.*,

$$\frac{\Delta \lambda}{\Delta l} = 4 \text{ (approx.)}$$

a fact observed previously by Gill and Donaldson.[1]

The circuit used is similar in principle to the well-known capacity coupled circuit of Colpit[2] usually represented as shown in Fig. 2. (See for the figures Ind. Jour. Phy, 1930, 349–354, It will easily be seen that C_1 and C_2 of Fig. 2 are replaced respectively by the interelectrode filament-plate and filament-grid capacities of Fig. 1. See for the figures Ind. Jour. Phy. 1930, 350), A rough solution of the condition for maintenance of the oscillations in such a circuit can be easily found according to the usual method,[3] *i. e.*,

$$r < \frac{L u_o}{(C_1+C_2)\, r_p} \qquad \dots \quad \dots \quad \dots \qquad (1)$$

where r is the resistance of the oscillatory circuit r_p the plate resistence of the valve. In the present experiment u_o the geometric amplification factor is about 25.

r_p is about...	2×10^4 ohms
L	10^{-6} henry
C_1+C_2	10^{-10} Farads

Hence for the maintenance of oscillations r should be less than about 10 ohms. Actually, in the experiment r is of the order of an ohm.

The capacity of the oscillatory circuit is formed of (1) the inter-electrode capacity between the grid and plate (C_o) (2) the self-capacity of the straight wires forming the inductance (C). These two capacities are in series and hence the effective capacity is

$$\frac{CC_o}{C+C_o} = \frac{C}{1+x}, \text{ where } x = \frac{C}{C_o}$$

1 Gill and Donaldson, Phil. Mag., 1926.

2 Morecroft, Principles of Radio Communication, p. 576.

3 Electrical Engineers, Data Book, E. B. Wadmore, Vol. III, p 150

the well-known formula for wave-length is

$$\lambda = 2\pi\sqrt{CL} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where C and L are measured in cms.

Inductance of a straight wire of length l is

$$= 2l\left[\log_e \frac{4l}{d} - 1\right] \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

Capacity of straight wire of length l is

$$= \frac{l}{2\log_e \frac{2l}{d}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (4)$$

where d is the diameter of the wire.

Using the above formulæ we have

$$\lambda = \frac{4\pi l}{\sqrt{1+x}} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

where $2l$ is the total length of the straight wires forming the inductance.

From the observed values of λ and l, x can be calculated from the above formula and hence we can find the value of C_0. The following table gives these results.

TABLE I.

Length l cms.	Wave-length λ_0 cm.	$x = \frac{C}{C_0}$	C cms.	C cms.
63·0	532	1·21	8·26	6·80
59·5	512	1·13	7·86	6·95
56·6	500	1·02	7·53	7·38
51·0	480	0·78	6·88	8·82
50·0	476	0·74	6·76	9·13
43·0	412	0·72	5·94	8·25

Mean value of C_0 the inter-eletrode grid-plate capacity = 7·9 cms. Considering the uncertainties attendent in these ultra short wave experiments the values of C_0 are fairly constant.

S. 2.

Coupling of two resonance circuits.

A circuit of the type shown in Fig. 3 was tried, (See for the figures Ind. Jour. Phy. 1930 p. 353) *i. e.*, it consisted in putting on the same valve two resonance circuits which were coupled to each other through the inter-electrode grid-plate capacity C_0. The length of the straight wires forming the two circuits was the same, *i. e.*, the two circuits were in resonance. Two Lecher wire systems were used which were respectively coupled to each of the oscillatory circuits. The wave-length measured on both the Lecher wires was found to be the same (this result being true even when the two oscillatory circuits had different natural frequencies) and it was observed that if one R. F. milliammeter was put on each of the Lecher wire systems, the maxima located and the milliammeters kept in that position, the deflection in the milliammeters on the Lecher wire (1) increased appreciably when the milliammeter was removed from the Lecher wire system, (2) and *vice versa*; these results are to be expected. In the following table is given the wave-length λ as observed in this case for different lengths l of the straight wires forming the inductance. In the second column are given the values of λ_0, *i. e.*, the wave-length when only one oscillatory circuit was present (as in the experiment of S. 1). The remaining columns of the table are referred to later.

TABLE II.

Length of the inductance wire l (cms.).	Wave-length when the two oscillatory circuits are present λ cms.	Wave-length when one oscillatory circuit is present λ cm.	$x = \frac{C}{C_0}$	C_0 the grid-plate capacity (cms.).
63·0	420	532	1·40	5·9
59·5	412	512	1·16	6·7
56·6	408	500	0·95	7·9
51·0	392	480	0·95	7·2
50·0	386	476	1·05	6·4

The theory[1] of the capacitative coupling of two circuits enables us to interpret the above results. An equivalent simplified diagram of the circuit in Fig. 3 is shown in Fig. 4. (See for the figures. Ind. Jour. Phy. 1930 p. 353-354.) The C_a and C_b of the circuit in Fig. 4 are the self capacities of the straight wires forming the inductances of the two oscillatory circuits of Fig. 3. L_a and L_b are the respective inductances of the two circuits.

The theory of capacitative coupling of two oscillatory circuits shows that if w_1 and w_2 be the natural frequencies of the circuits (1) and (2) respectively, *i. e.*,

$$w_1 = \sqrt{\frac{C_a+C_o}{C_aC_oL_a}},\quad w_2 = \sqrt{\frac{C_b+C_o}{C_bC_oL_b}} \quad \dots \quad \dots \quad (6)$$

We have the modified frequencies due to coupling

$$\sqrt{\frac{w_1^2+w_2^2 \pm \sqrt{(w_1^2-w_2^2)^2+4k^2w_1^2w_2^2}}{2}}$$

If $w_1 = w_2$ this reduces to $w_1\sqrt{1 \pm k}$

$$\text{where } k = \sqrt{\frac{C_aC_b}{(C_a+C_o)\,(C_b+C_o)}}$$

If L_a also equals L_b as is the case in the experiment described, then the two values of the frequency are,

$$w' = \sqrt{\frac{1}{LC}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

this frequency being independent of C_o,

$$w'' = \sqrt{\frac{2C+C_o}{LCC_o}} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (8)$$

$$L_a = L_b = L$$
$$C_a = C_b = C$$

It seems possible that in the experiment only the frequency w'' will be maintained and w' will be absent, for the maintenance of oscillations in the triode does depend upon the value of C_o while w' is independent of it. However, supposing that both are maintained and thus present

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1 Electrical Engineers' Data Book, p. 76; (for detailed treatment see Electrical Oscillations and Electric Waves—Pierce).

simultaneously, the two frequencies will beat [1] in the usual manner, the net result being a frequency $\frac{w'+w''}{2}$ modulated by the small frequency $\frac{w''-w'}{2}$

w—the observed frequency when both the oscillatory circuits are present—must then equal $\frac{w'+w''}{2}$

$$i.\,e.,\ w = \frac{w'+w''}{2} = \frac{w_0}{2}\left[\frac{1}{\sqrt{1+x}} + \sqrt{\frac{1+2x}{1+x}}\right] \ldots\ldots (9)$$

where $x = \frac{C}{C_0}$ and w_0 is the frequency when only one oscillatory circuit is present.

Now, in every case in these experiments w is observed to be greater than w_0 or $\lambda < \lambda_0$. If we try to solve equation (9) for x by putting for $\frac{w}{w_0} = \frac{\lambda_0}{\lambda}$, the observed value which is always greater than unity, we find that x becomes imaginary. This means, that if in any actual oscillatory circuit w' and w'' be both simultaneously present, w cannot exceed, it must be less than w_0. But as it is found that $w > w_0$, so we are justified in assuming that it is only w'' that is maintained and both w' and w'' are not present.

Hence we put,

$$w = w'' = w_0 \sqrt{\frac{1+2x}{1+x}} \ldots \ldots \ldots \ldots \ldots (10)$$

$$or\ \lambda = \lambda'' = \lambda_0 \sqrt{\frac{1+x}{1+2x}}$$

It is easily deduced from the equations already given that if the self-capacity of the wires forming the inductance of the oscillatory circuit be not taken into account, we should have

$$\frac{w}{w_0} = \frac{\lambda_0}{\lambda} = \sqrt{2} = 1{\cdot}42$$

but we get $\frac{\lambda_0}{\lambda} = 1{\cdot}26$ to $1{\cdot}22$ for different values of l. This shows that the self-capacity has to be taken into account.

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[1] Electrical Engineers' Data Book, p 75.

In fact, we can calculate the value of $x = \frac{C}{C_0}$ from the observed ratio $\frac{\lambda_0}{\lambda}$ [*eqn.* (10)] and knowing x we can find C_0. This is done in columns IV and V of Table II.

Thus these two different methods of finding C, *i. e., the simple resonance method of section 1 and the Coupling method of section 2 give values of* C_0 *that are in fair agreement.*

$C_0 = 7{\cdot}9$ cms. ... ... (method 1).

$C_0 = 6{\cdot}8$ cms. ... ... (method 2).

Morecroft[1] and others have found that for ordinary valves the grid-anode capacity lies between 3 to 15 cms.

The results obtaind in these experiments on the coupling of two circuits are in accordance with theory and it is hoped that a further study of them—the general case when the two circuits are not in resonance—will enale us to understand more fully the mechanism of the generation of oscillations in a triode and the theory of coupling itself.

We wish to express our grateful thanks to Prof. M. N. Saha, F.R.S., for his very kind interest and guidance in this work.

(Reprinted from The Indian Journal of Physics, Vol. IV, Part V.)

1 Electrical Engineers' Data Book, p. 161.

V—On the Application of the Ultra-short Wave Method to the Measurement of Small Capacities and Dielectric Constants.

By D. V. Gogate, and D. S. Kothari.

In a previous paper[1] we had described some experiments on the coupling of two resonant circuits to a triode and from a study of these coupled circuits, a method was suggested of determining the inter-electrode grid-plate capacity of a valve.

The present paper is divided into three sections. The first section deals with the location and measurement of the harmonics that are found to be invariably present along with the ultra-short waves. The conditions necessary for maximum oscillations have been studied.

The general theory of the coupling of two non-resonant circuits to the same valve is discussed in the second section and its application to the measurement of the inter-electrode grid-plate capacity of a valve is described.

In the third section is described the application of the ultra-short-wave method to the determination of the dielectric constants of certain liquids.

Sec. I.

Short waves were produced by using the oscillatory circuit already described in a previous paper.[2] The valve employed was a French power valve (anode volts up to 600 and fil. volts 5·5). It was also found possible to use two Philip's receiving valves in parallel in place of the valve, the valves 425 giving the best results. Two straight parallel bare eureka wires, S. W. G. No. 16, formed the inductance of the oscillatory circuit. These wires were connected, at one extremity, to the anode and grid pins of the valve and were bridged at the other extremity by a bye-pass condenser A lecher wire system coupled inductively to the oscillatory circuit was used to measure the wave-length of the short

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1 Ind. Jour. Phy., Vol. IV, pt. 5, 1930.

2 Lic. Cit.

waves produced, a thermo-milliammeter being employed as the detector of the current antinodes. The effect of varying the distance of the negative and of the filament wire 'w' from the grid 'G' was then tried. To do this, the end 'w' of the filament wire was moved along the grid-wire GX (fig. 1) (See for the figures Ind. Jour. Phy. 1930 p. 418) and the current intensity was noted by means of a thermo-milliammeter 'M' coupled inductively to the oscillatory circuit AYXG. It was found that the current intensity was proportional to the distance of 'w' from 'G' and became constant at the point 'X' where the grid-wire is joined to the condenser. As 'w' was moved beyond the point 'X' towards 'Q' there was no variation in the current intensity, showing thereby that the latter became constant from the point 'X' onwards. Similarly, when the end 'w' was taken very near 'G' the current fell to zero and remained zero even when 'w' was moved along the grid-wire GN on the other side of 'G'. These facts are represented in fig. 2 (See for the figars Ind. Jour. Phy. 1930 p. 419). where the straight line portion of the curve shows that the current intensity is proportional to the distance of 'w' from 'G' for quite a big range.

It was also found that the distance of the end 'w' from the grid did not affect in any way the frequency of the waves produced by the oscillatory circuit.

In the production of these ultra-short waves it was only the fundamentals that were studied in the previous papers, the harmonics were however found to be invariably present and their location and measurement were consequently undertaken

One method[1] of studying these harmonics, which is quite common, is to connect the thermo-milliammeter to the ends of the lecher wires near the oscillatory circuits. By means

1 Blake and Ruppersberg, Phy. Rev., Vol. XXXII, (1911).
Blake and Sheard, " " " " (1911).
" " " " " " III, (1914).
" " " " " " IX, (1917).

of a piece of bare wire, the lecher wire system is then short-circuited at different points along its length and the corresponding changes in the current noted. This has been done and the values of current strength are plotted against the distance of the short circuiting wire from the milliammeter, fig. 3 (A). (See for the figure Ind Jour. Phy. 1930. p. 420) The graph clearly shows the fundamental at the distance of 550 cms. accompanied by different harmonics.

The harmonics were also studied by another method. The thermo-milliammeter was joined in series with one of the wire 'L' of the lecher system (fig. 4 See for the figure Ind Jour. Phy 1930. p. 421) kept inductively coupled to the oscillatory circuit by a loop passing round a wooden pulley 'P' fixed at a short distance above the circuit. At their extremity, the lecher wires were wound in opposite directions upon a cylindrical ebonite rod and weights were hung from each end of the wires to keep the latter straight. By means of this arrangement it was made possible to measure the current intensity at every point of the lecher-wire system by simply turning the ebonite rod about its axis. At a distance of 550 cms. from the pulley, where maximum current was noted in a preliminary experiment, the lecher wire system was kept short-circuited by a piece of bare wire and then by turning the ebonite rod about its axis, the thermo-milliammeter was moved along the length of the lecher-wires.

In this way the current-strength was measured at different points along the lecher-wire system and a graph (fig. 3 B.) (See for the figure Ind. Jour. Phy. 1930 p. 421). was plotted with current against distance from the wooden pulley. This graph shows clearly the presence of two chief antinodes at the distances of 0 and 550 cms. respectively together with the other harmonics that were present.

Sec. 2.

The experiments on the coupling of oscillatory circuits were tried with circuits of different natural frequencies.

After measuring the wave-length of the short waves produced with one oscillatory circuit (length of parallel wires 63 cms.) *attached to the valve, a second circuit,* whose *inductance and capacity* were different from those of the *first circuit, i. e.,* which was not in resonance with the first circuit, was coupled to the valve on the other side, *fig.* 5, (See *for* the figure Ind. Jour. Phy. 1930-422) and the wave-length again measured. The first circuit was now removed and the wave-length determined with only the second circuit present. This process was repeated with circuits of different natural frequencies, the first circuit (length of parallel wires 63 cms.) beidg kept fixed. In this way different readings were taken and the values of wave-lengths obtained have been given in columns, 3, 4, and 5 of table I.

For a theoretical discussion of the coupled circuits let us represent the oscillatory circuit of fig. 5 by its equivalent simplified diagram (fig. 6). (See for the figure Ind. Jour. Phy. 1930-422)

The C_1 and C_2 of the circuit of fig. 6 (See for the fig. Ind Jour. phy. 1930 p. 423) are the self capacities of the straight wires forming the inductances of the oscillatory circuits (1) and (2) of fig. 5. L_1 and L_2 are the inductances of the two circuits respectively.

Let an e. m. f. be supposed to be introduced at X and the total impedance of the two circuits obtained and equated to zero. The solution of the quartic equation in w thus obtained gives the resonant frequencies of the whole system.

$$\frac{1}{Z_2} = JC_0 w + \frac{1}{JL_2 w + \frac{1}{JwC_2}} \quad \ldots \quad \ldots \quad (1)$$

where Z_2 is the impedance of the circuit (2)

$$\therefore Z_2 = \frac{1-w^2L_2C_2}{JC_0w - Jw^3C_0L_2C_2 + JwC_2} \quad \ldots \quad \ldots \quad (2)$$

$$\therefore \text{ Total impedance} = \frac{1 - w^2 L_2 C_2}{JC_0 w - Jw^3 C_0 L_2 C_2 + Jw C_2} + \frac{1}{JC_1 w} + JL_1 w = 0 \quad \dots \quad \dots \quad (3)$$

$$\therefore w^4 - w^2 \left[w_1^2 + w_2^2 \right] + \frac{C_1 + C_0 + C_2}{L_1 L_2 C_1 C_2 C_0} = 0 \quad \dots \quad (4)$$

where $$w_1^2 = \frac{C_1 + C_0}{L_1 C_1 C_0} \quad \dots \quad (5)$$

and $$w_2^2 = \frac{C_2 + C_0}{L_2 C_2 C_0} \quad \dots \quad (6)$$

w_1 and w_2 being the natural frequencies of the two circuits respectively.

On solving this quartic equation,

we have,

$$w = \sqrt{\frac{w_1^2 + w_2^2 - \sqrt{(w_1^2 - w_2^2)^2 + 4k^2 w_1^2 w_2^2}}{2}} \quad \dots \quad (7)$$

where, $$k = \sqrt{\frac{C_1 C_2}{(C_1 + C_0)(C_2 + C_0)}} \quad \dots \quad (8)$$

From the values of wave-lengths given in table I, all the frequencies, w, w_1 and w_2 can be calculated and then the value of k can be determined from the above formula.

The self-capacity of the straight wires forming the oscillatory circuits is calculated from the relation[1]:—

$$C = \frac{l}{2 \log_e \frac{2l}{d}} \quad \dots \quad (9)$$

where, l = length of the wire,

and d = diameter of the wire.

In this way knowing the values of C_1, C_2 and k, the value of C_0, the inter-electrode grid-plate capacity of the valve can be calculated from the quadratic equation (8). This has been done in table I where the first two columns give the lengths of the straight wires forming the oscillatory circuits.

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1 Electrical Engineer's Data Book, E. B. Wedmare, Vol. III.

TABLE I.

l_1 in cms.	l_2 in cms.	Wave-length with both circuits present λ in cms.	Wave-length with first osci. circuit present λ_1 in cms.	Wave-length with second osci. circuit present λ_2 in cms.	C_0 in cms.
63	84	458	528	636	7·76
,,	78	448	,,	602	7·35
,,	70	438	,,	582	6·30
,,	66	424	,,	548	5·60
,,	63	416	,,	528	5·90
,,	60	412	,,	512	5·85
,,	55	402	,,	476	6·80
,,	50	386	,,	448	6·35

Mean value of C_0 = 6·5 cms.

It will be seen from the above table that the values of C_0 are fairly constant. It may also be noted that the mean value of C_0'' obtained by this method agrees fairly well with that given by the resonance method.[1]

Sec, 3.

Measurement of Dielectric Constant.

The method of ultra-short waves was also applied to the measurement of dielectric constant. For this purpose the circuit of fig. 7 (See for the figures Ind. Jour. Phy. 1930 p. 426) was used. The wires BB on the right side are bent at right angles as shown in the fig. The vertical portions of these wires which are equal in length are dipped in a glass vessel in which different liquids whose dielectric constants are to be measured may be filled.

The principle of the method is to measure the change in wave-length produced by the change in capacity of the

[1] *Loc. cit.* p. 417 above.

vertical portions of the wires when they are dipped in different liquids. From the change in wave-length thus produced, the dielectric constants of the liquids can be determined.

Let k be the capacity of the two parallel vertical portions of the wires in air. Then the wave-length of the oscillatory circuit is given by :

$$\lambda = 2\pi\sqrt{L(C+k)} \qquad \text{... (10)}$$

where, L = inductance of the oscillatory circuit,
and C = capacity of the oscillatory circuit.

$$\therefore \lambda^2 = 4\pi^2 L(C+k).$$

Differentiating, we get,

$$2\lambda d\lambda = 4\pi^2 L\, dk$$

$$\text{or} \quad dk = \frac{\lambda d\lambda}{2\pi^2 L}. \qquad \text{... (11)}$$

All the quantities in the right hand expression of equation (11) being known, dk can be calculated.

Now, if l = length of the wire dipped in the liquid,
D = distance between the two dipping wires,
d = diameter of the wire.

then the capacity formed by the two vertical portions of the wires is given by[1] :—

$$k = \frac{\cdot 109 l}{\log_{10}\left(\frac{2D}{d}\right)} \qquad \text{... (12)}$$

with air as the dielectric.

When the wires are dipped in a liquid of dielectric constant δ, the capacity is given by:[2]—

$$k = \frac{\delta \times \cdot 109 l}{\log_{10}\left(\frac{D}{d}\right)} \qquad \text{... (13)}$$

[1] Fleming's Pocket Book.
[2] .. .. ..

∴ change in capacity

$$dk = (\delta - 1)\ \frac{\cdot 100 l}{\log_{10}(D/d)} \quad \ldots \quad (14)$$

Substituting the value of dk obtained from equation (11), δ can be calculated.

$$\frac{\lambda d\lambda}{2\pi^2 L} = (\delta - 1)\ \frac{\cdot 109 l}{\log_{10}(D/d)} \quad \ldots \quad (15)$$

Length of the wires of the oscillatory circuit 25 cms.
Distance between the two wires of the osci. circuit 8·5 cms.
Diameter of the wire 0·123 cm.
Distance between the two wires dipping 1·0 „
Valves used :—Philips A 425; Two in parallel.

TABLE II.*

Dielectric	Length dipping	Wave-length	Dielectric Constant
Air	...	603 cms.	...
Kerosene oil	3·9 cms.	615 „	4·06
Petrol	3·3 „	613 „	2·8

* We are indebted to Messrs. Jaichandra and B. D. Pant for these observations.

Calculations :—

(1) Kerosene oil.

$$dk = \frac{\lambda d\lambda}{2\pi^2 L}\ ; \qquad \begin{aligned} L &= 4l \log_e (2D/d) \\ &= 4 \times 25 \times 2\cdot 3 \log (17/\cdot 123) \\ &= 492\cdot 2 \text{ cms.} \end{aligned}$$

$$\text{Again, } dk = \frac{l \times \cdot 109}{\log. \frac{2D}{d}}\ (\delta - 1)$$

∴ $\delta = 4\cdot 06$

(2) Petrol.

Similarly, for petrol we get $\delta = 2\cdot 8$.

The experimental procedure can be varied. The R. F. milliammeter is kept fixed on the lecher wires and a graph is plotted between the lengths of the wires VV and the current in the milliammeter. The wires VV are then dipped in the liquid and from the change of current in the milliammeter which is kept fixed on the lecher wires, the change in the capacity of the wires VV is noted by means of the graph already plotted This change in capacity gives immediately the dielectric constant. This procedure gives more accurate results and is better adapted to the study of the temperature variation of the dielectric constant which is to form the subject of a subsequent communication.

Our best thanks are due to Prof. M. N. Saha, F.R.S., for kind interest in this work.

Baroda College and Allahabad University,

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VI—On the Measurement of Quantity of Light by the Photo-Electric Cell.

By D. V. Gogate and D. S. Kothari.

The application of the photo-electric cell in the measurement of intensity of light is well-known. The present paper deals with the use of the cell for the determination of the quantity of light. These two uses of the photo-electric cell correspond to the use of a galvanometer for measuring current and quantity of electricity respectively.

If a source of candle power (C. P.) be placed at a distance r from a cell of area A, the luminous flux received by the cell will be $\frac{(C.P.)}{r^2}$ A lumens. If this causes a galvanometer

deflection of θ divisions, then we have,

$$K \frac{(C.P.)}{r^2} A = S_c \theta \quad \ldots \quad (1)$$

where S_c represents the currents sensitivity of the galvanometer and K is a constant.

If light from the source of candle power (C.P.) be allowed to fall on the cell for a time Δt, then,

$$S_q \theta' = K'Q = K'AI \Delta t$$

where S_q denotes the ballistic sensitivity of the galvanometer, θ', the kick observed, Q, the quantity and I, the intensity of light. Therefore,

$$S_q \theta' = K'A \frac{(C.P.)}{r^2} \Delta t \quad \ldots \quad (2)$$

The cell used is the Westinghouse Photo-electric cell (Type P.A. I). It consists of a disc of copper oxidised on one side by a special treatment to cuprous oxide.

To test the relation (I) the cell was placed at different distances from a 16 volt 32 watt lamp and the corresponding deflection θ in the galvanometer was observed in each case. It was found that $r^2 \theta$ was nearly constant and we obtained for K the value $7{\cdot}5 \times 10^{-6}$ amperes per lumen.

The relation (2) was verified by allowing the lamp to fall vertically from different heights in front of the photo-electric cell and noting the corresponding kicks in the galvanometer. For this purpose the lamp was fixed in a thick card-board sheet which was allowed to fall smoothly in a vertical plane distant about 10 cms. from the photo-electric cell by means of pulleys and falling weights, The illumination of the photo-electric cell by the falling lamp is maximum when it is just in front of it, but even when it is a couple of centimetres away from this position, on either side, the cell receives an appreciable amount of light. The "effective

value " Δx of this range was determined by plotting a graph between the steady deflection in the galvanometer and the height of the lamp. The area enclosed by this graph divided by the maximum value of the deflection gives the value for Δx. The duration of exposure Δt was then calculated from the relation,

$$\Delta t = \frac{\Delta x}{\sqrt{2fx}}$$

where, f is the acceleration of the system (lamp, weights, etc.) and x denotes the height of the lamp from the cell. Thus finally, we have,

$$S_q \theta' = K'A \frac{(C.P.)}{r^2} \cdot \frac{\Delta x}{\sqrt{2fx}} \qquad ...(3)$$

Our experiments gave the value for K' to be 6×10^{-6} coulombs per lumen-second. From the known properties of the photo-electric cell one should expect this value to agree with the value of K in equation (I). Our experiments show that K' is slightly less than K.

For these experiments the cell was connected directly to the galvanometer. We now propose to introduce an amplifier in between and then use the cell for measuring the quantity of light in lightening discharge and other similar phenomena.

It may be of interest to note here that the internal resistance of the photo-electric cell, as given by the makers, is 1800 ohms. It is, however, found to vary with the current passing in the cell. * When the direction of the current is from copper to cuprous oxide (the same as the direction of

* The current was always kept less than about two milli-amps. in accordance with the instructions of the manufacturers,

the photo-electric current),† the resistance is found to increase with the current and varies from about 350 to 1700 ohms. The latter value corresponds to a current of about 1.5 milli-amperes in the cell. On further increase in the current through the cell, its resistance begins to decrease and is unsteady. When the direction of the current in the cell is from cuprous oxide to copper (the same as the direction of the rectified current),† the resistance decreases with increase of current and varies from about 300 to 140 ohms.

Physics Laboratory,
University of Delhi.

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VII—Physics of " Smell."

BY D. V. GOGATE AND D. S. KOTHARI.

Prof. Bohr in his recent address‡ on ' Life and Light ' has emphasised the peculiar organisation of living beings with a view to understanding their essential characteristics. This organisation exhibits typical atomistic and quantum traits combined with the ordinary mechanical characteristics, in a manner having no counterpart in inorganic matter.

As an illustration of the refinement to which this organisation is developed, Prof. Bohr has considered the case of the human eye. The eye is an ideal and perfect optical instrument inasmuch as its resolving power and its sensitiveness have reached the limit imposed by the wave and quantum nature of light. It has been found that the eye can be stimulated by a few light quantam (or possibly a single light quantum ?). Further the optical resolving power

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† The direction of the generated current in the photo-electric cell is from copper to cuprous oxide, *i. e*, opposite to the direction of the rectified current, when the combination Cu-Cu_2O is used as a rectifier.

‡ Nature, March 25 and April 1, 1933.

(5/d") where d is the aperture of the eyelens in inches) and the physiological resolving power (angle subtended by the "cone" in the retina at the eyelens) of the eye are almost the same. This perfection of the eye naturally leads one to expect that the other organs also may reveal similar characteristics, the study of which will greatly help in establishing the relation between organic evolution and physics.

A consideration of the construction and function of the nose may also afford another interesting example. The human nose appears to be very sensative to smell. However Physics corresponding to the sensation of smell does not exist at all, though physics of the eye and the ear (being simpler) has developed so much.

It is of interest to see whether the sensitiveness of the nose has also reached a limit imposed by the atomic character of substances giving rise to the sensation of smell; i. e., whether the sensation of smell can be excited even when there be present a few molecules (or a single molecule ?) of an intensely smelling substance. Any data that might be obtained in this connection are bound to be helpful in the study of the evolution of senses. It is intended to make some tests on this point and we shall be glad to receive information on data concerning this if already obtained.

(Reprinted from " Current Science " Vol. II, No. 6 December 1933.)

VIII—On the theory of the Surface-tension of Liquid Metals.

By D. V. Gogate and D. S. Kothari.

It is well-known that the surface-tension of liquid metals is very much greater than that of other substances. For example the surface-tension of Au, Pb, Hg etc. is of the order of five hundred while for non-metals like sulphur, petrol etc. it is only about fifty. We have worked out, on the free-electron model of Sommerfeld and taking into account the Coulomb forces between ions and free-electrons and the Fermi Dirac distribution law for electrons, a theory of surface-tension of liquid metals. By a straight-forward application of the theory, we obtain the formula for surface-tension S,

$$S = \frac{1}{32} \frac{h^2 \beta}{\pi m \, m_H^{\frac{4}{3}}} \left(\frac{P}{A}\right)^{\frac{4}{3}} + \frac{T}{4} \frac{dS}{dT}$$

Where β is a constant, very nearly unity, but its exact value is to some extent uncertain; P is the density, A the atomic weight, T the absolute temperature, m the mass of the electron and m_H the mass of proton. Taking β as unity and for the present neglecting the small correction due to the term $\frac{T}{4}\frac{dS}{dT}$ we give below the calculated and observed values for a few metals. Better agreement is obtained by taking $\beta = 0.9$

Metal	S (calc) with $\beta=1$	S (calc) with $\beta=0.9$	S (observed). Dynes/cm.
Na	329	294	294
Ag	924	825	800
Pb	498	445	444
Cd	781	697	630
Hg	668	596	465

The observed values are taken from the International Critical Tables. It may be noted that these values are not very reliable as different observers sometimes give widely different results; for example, in the case of Hg, Kaye and Laby's Tables (1932) give after Quincke the value 547. The value of the correction term $\frac{T}{4}\frac{dS}{dT}$ is uncertain as the data for $\frac{dS}{dT}$ are very meagre and even so not available in all cases. To obtain an idea of this correction we take the case of Hg where $\frac{dS}{dT}$ is found to be nearly 0.4 and so $\frac{T\,dS}{4dT}$ will be about 30.

The above theory also explains some important properties of thin films i. e. the electric conductivity of very thin films is smaller than the conductivity of metal in bulk by a factor of (5–10). The full paper will shortly appear in Phil. Mag.

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IX—A Note on the theory of Viscosity of Liquid Metals.

A theory of the viscosity of liquids on simple classical lines has been recently put forward by Prof. Andrade. Assuming that the liquid molecules retain sufficient of the crystalline character which they had in the solid state and possess a frequency of vibration very nearly equal to the frequency in the solid state at the melting point, and on replacing this characteristic frequency in terms of the melting point by using Lindeman's semi-empirical formula, he obtains the formula

$$n = \tfrac{4}{3}\, C\, \frac{(A\, T_m)^{\frac{1}{2}}}{(N\, V_A)^{\frac{2}{3}}} = 5.1 \times 10^{-4}\, \frac{(A\, T_m)^{\frac{1}{2}}}{V_A^{\frac{2}{3}}} \quad \ldots \quad (1)$$

where n is the viscosity, A is the atomic weight, N the Avogadro's number, T_m the melting point and V_A the volume of a gram-atom at the temperature T_m.

In view of the recent investigations[a] into the properties of liquid metals it may be of interest to deduce a formula for viscosity of metals in the liquid state in a slightly different form. Following Andrade, we take the liquid metal near the melting point, as still possessing the lattice structure which was characteristic of it in the solid state. The Debye or rather Einstein characteristic frequency is, of coure, different in the liquid state and in fact,

$$\left(\frac{V_L}{V_S}\right)^3 = e - \frac{L}{kT}$$

Where L is the latent heat.

If the liquid molecules vibrate with a frequenoy V we get, with Andrade, $n = \frac{4}{3}\frac{Vm}{l}$ where l is the average distance between the centres of molecules. Putting $\beta l = n^{-\frac{1}{3}}$ where n is the number of molecules per unit volume and β is a constant, $n = \frac{4}{3} \mathrm{B} Vmn^{\frac{1}{3}}$. If P denotes the density, A the atomic weight and m_{H} the mass of the hydrogen atom, we have,

$$n = \frac{\mathrm{P}}{\mathrm{A}m_{\mathrm{H}}} \text{ and } n = \frac{4}{3}\,\mathrm{B}V\left(\frac{\mathrm{P}}{\mathrm{A}}\right)^{\frac{1}{3}} \mathrm{A}m_{\mathrm{H}}^{\frac{2}{3}}$$

If now, we put $hv = k\,\theta_L$ or $v = \frac{k}{h}\theta_L$ where K represents Baltzmann's constant, h is Planck's constant, and θ_L is the Debye characteristic temperature, we get

$$n = \frac{4}{3}\beta\,\frac{k}{h}\,m_{\mathrm{H}}^{\frac{2}{3}}\,\mathrm{A}\left(\frac{\mathrm{P}}{\mathrm{A}}\right)^{\frac{1}{3}}\theta_L \qquad \dots \quad (2)$$

The values of viscosity calculated from the above formula and the observed values of viscosity of certain liquid metals for which published experimental data exist are shown in the following table :—

Liquid metal.	n cal. with $\beta = 23$	n obs.
Cd	·024	> ·018
Hg	·023	·021
Cu	·032	·038
Pb	·023	·028

It will be seen from the above table that the agreement between the calculated and observed values is fair, considering the large discrepancies between the values of viscosities obtained by different observers and also the approximate nature of the theory. According to Andrade's formula the agreement between theory and experiment for the four liquid metals Hg, Pb, Sn, and Cu is, no doubt, very satisfactory; but this is to a certain extent a chance coincidence. As Andrade himself observes, "No great emphasis is placed by the writer on the surprising closeness of the agreement for the four metals, which is within 10 per cent. or less, for this agreement depends upon the exact value given to the constant in formula (1)". In formula (2) the agreement depends upon the value of the constant β and upon the crystal structure of the metal.

Again, it is more usual and theoretically better to express the characteristic frequency in terms of the Debye temperature θ_L as we have done in (2) and not in terms of the melting point, as in (1). In this we are also following Mott's recent use in his paper[3] on the resistance of liquid metals.

Baroda College,
Gujrat.

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(1) Phil. Mag. 17, 497, 1934.
(2) Proc. Roy. Soc. 146, 465, 1934.
(3) *Loc. Cit.*

X—The present position regarding the Theories about the Nature of Active Nitrogen.

By C. R. Dhodapkar.

In 1900 E. P. Lewis observed [2,7] that nitrogen could be stimulated by an electric discharge to emit a bright yellow glow which continued for some time even after the discharge had ceased. He photographed the infra-red portion of the spectrum and made a number of spectroscopic observations on the glowing nitrogen. Lord Rayleigh, who investigated the phenomenon in a more general and systematic way, discovered that the glowing gas had remarkable spectroscopic and chemical properties and named it 'Active Nitrogen'. Active Nitrogen could be produced in a number of ways. Kaplan[10] produced it by passing condensed discharge through air at 0·5 m. m. Herzberg showed that it was possible to produce active nitrogen in which the percentage of nitrogen varied from 100 per cent to 40 per cent. Hagenbach and Frey [13] showed that glowing active nitrogen could be produced by passing condensed discharge through air at 10 m.m. The spectra observed by all these authors were the same as that obtained from active nitrogen that has been produced from almost pure nitrogen. It is, however, our experience that active nitrogen, as produced from almost pure nitrogen is the most intense.

N_2 molecule the emitter.

It may be mentioned, as a passing remark that a line spectrum due to the nitrogen atom is known, but is not shown by active nitrogen. Wien showed the emitting system of the nitrogen first positive bands to be uncharged. He allowed a stream of luminous gas to flow out of a canal tube into a space where a vacuum of the order 10^{-3} to 10^{-4} m.m. is continuously maintained by a number of diffusion pumps. In this space the gas is allowed to pass between two parallel plates

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* The presence of a slight impurity is very essential for the production of active nitrogen.

which are maintained at a small distance apart at a constant difference of potential. The spectrum of the luminous slit-like region is photographed. Particles which are uncharged showed straight spectral lines, while lines due to charged particles are bent one way or the other. The vaccum in the space is so high that no collision takes place amongst the particles. Further Rayleigh was unable to condense anything which might indicate the existence of a body such as N_3. It seems fairly certain therefore, that the characteristic luminescence is emitted by simple diatomic nitrogen molecules in some *unusual* State.

Properties and Phenomena observed.

As has been said before, active nitrogen has remarkable spectroscopic and chemical properties. Its most conspicuous features are green, yellow and red bands*; the yellow ones, being usually the brightest, give the glow a yellow colour. The passage of a weak discharge through active nitrogen excites the fourth positive bands, but results, as was pointed out by Strutt, in the partial destruction of the afterglow. Heat has a peculiar effect on the afterglow. If a stream of glowing gas is passed through a tube which is moderately heated, the glow is locally extinguished, although it is still able to excite sodium atoms to the emission of the yellow doublet ([11, 12, 13]). If on the other hand, it is carried through a tube immersed in liquid air, it glows with increased luminosity. Active nitrogen reacts with metals, non-metals and compound bodies in a remarkable way. It excites the D and sometimes tne green doublet of sodium, and also the line spectra of Cd, Mg, Hg, K, Zn, P, Th. It changes yellow phosphorus to red, forms a transparent green deposit with sulphur and reacts with several non-

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* The system of bands referred to are the N_2 bands in the spectrum of active nitrogen belonging to the First positive System $B^3\pi \rightarrow A^3\Sigma$. See Dr, Jevon's Report on Spectra, P. 206.

metals such as iodine, arsenic, etc. The reaction with nitric oxide is important; the gases interact with the production of a greenish flame, the evolution of heat and the formation of nitrogen peroxide and nitrogen. It develops the band spectra of compounds when they are vaporised in it, giving in many cases spectra of substances too unstable to be examined at the temperatured of Bunsen flame. In fact this simplified development of the band structure constitutes a great advantage of active nitrogen over the arc or the spark in the study of band-spectra. It is true that the band system developed in this way often differs considerably in appearance from the same system developed in arc or spark on account of a radical change in the intensity distribution as regards both the intensity of the lines in each band and the relative intensities of the bands of the system. In its interaction with other substances, active nitrogen is able to transfer to atoms and molecules amounts of energy up to, but not exceeding, 9·4 though amounts up to 10·4 volts may be transferred under certain conditions[8].

Various theories have been advanced to explain the nature of active nitrogen, and the mechanism of its formation and decay, but as yet there is no theory which can explain all the characteristics, the properties, and the reactions of active nitrogen, The present is an attempt to throw some more light on this problem which still awaits a more satisfactory solution.

It has been said above that the presence of some impurity is essential for the production of active nitrogen. The emission of the spectrum of the afterglow is one in which nitrogen alone is concerned; the impurity simply plays the part of a catalytic agent, and is involved in no other way, for the spectrum is identical whether the impurity is oxygen, methane or any other gas.

We now come to the consideration of the mechanism by which active nitrogen is produced and suffers decay. We

have obviously three possible views before us; (a) atomic nitrogen emerges from the discharge and then recombination takes place to give the molecules which are at an energy level high enough to give the known spectrum, (b) nitrogen atoms emerge from the discharge and in a triple collision that follows combine to form a normal molecule, the energy involved in the recombination process being utilised to excite a third partner, the normal molecule involved in the collision, to a higher energy level, (c) molecules of nitrogen excited in the discharge to a higher energy level are 'metastable'; that is, they have considerable life and can continue to exist for some time after leaving the discharge.

If we now assume (a) to be the possible mechanism, a spectroscopic difficulty arises, in that we should expect a certain amount of continuous spectrum as a result of the recombination of free atoms. There is yet another difficulty; unless the two atoms meet in a triple collision with a third molecule which can remove the energy liberated in the union of two atoms, there is every reason to expect that the energy so liberated in the recombination procees would again break asunder the newly formed molecule into atoms. Thus if the mechanism involves the union of atoms into molecules, that recombination can take place only in triple collisions.

Triple Collision.

One of the main differences of the condensed and the uncondensed discharge in nitrogen is the excitation of the fourth positive group in the former, the null (0, 0) band in this group requiring about 14·8 volts for its excitation. In order to obtain active nitrogen in any appreciable quantity, it is very necessary to use a condensed discharge. All the known fourth positive bands originate on the D level that has zero as its vibrational quantum number (*). Bands arising on higher D levels have not been observed, suggesting that the binding in this state is so weak that dissociation occurs quite readily. These facts suggested to Sponer the

(*) Dr Jevon's report on band-spectra, p. 77.

following hypothesis[14] regarding the nature of active nitrogen. A discharge in which the molecules are on the brink of dissociation should according to Sponer abound in atoms. This and the long life of active nitrogen and its behaviour in the presence of catalysts suggest with reasonable certainty that active nitrogen is composed of normal atoms and molecules. The characteristic visible afterglow is emitted as a result of triple collision between two atoms and one molecule; the energy liberated during the recombination process of two atoms is in many cases sufficient to raise the third partner to the vibration level corresponding to quantum number twelve of the B state. Dr. Sponer's estimate of the dissociation energy[14] was 11·5 volts, the energy which is necessary to excite these bands. But it is now difficult by her theory to account for the afterglow bands, as the work of dissociation of the nitrogen molecule has recently been estimated at about 7·34 volts† (the figure now accepted by all). Secondly her theory is unable to explain the exceptional enhancement of the abnds corresponding to vibration numbers 11 and 6 in the upper $B^3\pi$ state.

Before we go on to consider the mechanism (c), we will just consider the selection rules for electronic transitions for band-systems. They are

(i) Change of S=0 usually or ± 1 less frequently; i. e. change of multiplicity=0 usually or ± 2 less frequently.

(ii) Change of = 0 or ± 1; Change of Σ = 0.

(iii) Change of λ for 'emission' electron= 0 or ± 1.

(†) Sponer and Herzberg determined the value of dissociation energy to be 7·34 volts (Zeits fur Phys-Chem 26 B, 1, 1934) although the accuracy of their result is questioned by Appleyard, Thomson and Williams (Nature 134, 322, 1934) The figure 7·3 is now strongly supported by Maier-Leibnitz and Sponer (Z P 89, 431, 1934), Mulliken (P R, 46, 144, 1934) and Buttenbender and Herzberg (Ann der Phys, 21, 577, 1935) and some of Kaplan's 1934 notes.

(iv) Of the three conceivable transitions between three given electronic states, all may take place in a compound molecule, but not more than two in an elementary molecule.

This extra restriction in the case of elementary molecules. was interpreted by an application of the quantum mechanics, The elementary states of an elementary molecule are classed theoretically as 'even' or " odd " according as the sum of the individual l-values for all electrons is even or odd, exactly as in the case of atomic states. Transitions occur only between states of opposite character, g $\rightarrow$ u and and u $\rightarrow$ g, and this rule, which is exactly the same for atoms, applies rigorously to elementary molecules. The molecule which emits the afterglow bands is N_2, an elementary molecule. The N_2 states X, A, a, B and C are classed as $X'\Sigma g$, $A^3\Sigma u$, $a'\ \pi/u$, $B^3\ \pi/g$, and $C^3\ \pi/u$ respectively. The observed system C $\rightarrow$ B (2nd positive), B $\rightarrow$ A (first positive) and A $\rightarrow$ X Vegard's Σ system, are all according to this selection rule. But A is a triplet level, while X is a singlet level. The transition A $\rightarrow$ X is very feeble because of the inter-multiplicity. A is thus a metastable state to a certain extent.

Further from the Hund theory, we can predict the lowest three terms of atomic nitrogen to be ^4S, ^2D, and ^2P, where ^4S term is a normal one, and ^2D and ^2P are metastable states. The difference ^2D—^4S is found from Hopfield's data on the ionization limits of N 1 to be 2·37 volts. The difference ^2P—^4S has been interpreted from the spectrum of O II and is found to be 3-56 volts,

Cario and Kaplan[18] considered that beside normal atoms and molecules, active nitrogen contains non-vibrating metastable molecules in the $A^3\Sigma$ state corresponding to an energy of 8·2 volts* in addition to two kinds of metastable

* State A Σ was at that time supposed to have electronic energy of about 8·2 volts, but has recently been shown to have only 6·14. The state $B^3\pi$ has therefore 7·31 volts.

atoms in ^2D and ^2P state corresponding to energies of 2·37 and 3·56 volts respectively. They explain the special enhancement of the bands corresponding to quantum numbers 11 and 6 in $B^3\pi/$ state as a result of collision between metastable atoms and the metastable molecules, for the energies necessary to excite these bands are very nearly equal to 11·5 (8·2+3·56) and 10·5 (8·2+2·37) volts respectively. With this theory the ' dark modification ' which can still excite D lines of sodium, the emission of the afterglow bands, as well as other properties could be satisfactorily explained.

Assuming that in active nitrogen, metastable molecules and metastable atoms occur at proper concentration, the so-called resonance effect in the metallic spectra should be expected to occur, that is to say the lines corresponding to an excitation energy greater than that of the metastable molecules (8·2 volts) will be extremely weak in comporison with those which have their excitation energies equal to 8·2, 2·37, and 3·56, or smaller than 8·2. The more intense the lines appear, the nearer their excitation energies to 8·2, 2·37, 3·56, volts. No special enhancement of such lines was observed in the metallic spectra observed by several experimenters.

POTASSIUM *

Line observed	Excitation energy	Remark.
1^2S-4^2P	3·58	No special enhancement.
2^2P-4^2D	3·38	,,
2^2P-3^2S	3·38	,,
Caesium *		
1^2S-5^2P	3·42	,,
2^2S-6^2P	3·55	,,
2^2P-6^2D	3·43	,,
2^2P-7^2D	3·56	,,
Mercury *		
2^3P-2^1S	7·89	,,

* The Science Reports of the Tohoku Univ. vol. 21, No. 4, p. 557, 1932.

It is to be concluded from the above that as there is no evidence of resonance enhancements, the concentrations of such metastable atoms and molecules, if they exist at all in active nitrogen, is negligible. On the other hand, it is generally observed that in active nitrogen, lines of lower excitational energy appear, without any exception, to be more intense than those of higher excitational energy, and that the decreasing rate of the intensities of the lines with the increase of term number is more rapid in this case than in any other case of excitation. (3, 4, 6). Again the long life of active nitrogen which is its important feature cannot be explained by the existence of metastable atoms and molecules. Besides from the results of exhaustive experiments carried out by Herzberg[16], Kneser,[1] Wrede[17] Bay and Steiner[21] it is at present generally accepted that active nitrogen is Composed of nitrogen atoms and that its main properties are natural consequences of its atomic nature.

J. Okubo and H. Hamada[9] accepted Sponer's hypothesis regarding the nature of active nitrogen, namely that active nitrogen is composed of normal atoms and molecules. They have made, however, two assumptions to explain the observed results and properties of active nitrogen. The assume in the first instance that in the vibrational states with $v''=8$ in the metastable $A^3\Sigma$ state and that corresponding to $v'=6$ in the upper $B^3\pi$ state, the near-nuclear turning points have the same nuclear distance as the nuclear separation between the nuclei in the normal $X^1\Sigma$ molecular state. Secondly they assume that with the exception of neutral unexcited atoms and molecules, molecules corresponding to quantum numbers 7 or 8 of the metastable $A^3\Sigma$ state are the most numerous. With these assumptions, they suggest that the nitrogen molecules are excited to the required energy levels in two steps, the first being the excitation to the metastable $A^3\Sigma\ v\ 8$ state and the second to the $B^3\pi\ v\ 11$ and $B^3\pi\ v\ 8$. Most of the properties of active nitrogen can then be explained by this modified view.

It is however doubtful if the two assumptions made have really the experimental backing they need. The Morse function that they have used to find the near-nuclear distances gives the values very approximately. Secondly it will also be seen from the diagram (see Journal of the University of Bombay September, 1935) that the potential energy curves for $B^3\pi$ and $A^3\Sigma$ states on the left hand side run almost steep and it will be equally accurate to say that the nuclear distances for some quantum numbers other than 8 for the $A^3\Sigma$ state and those for some quantum numbers other than 6 for $B^3\pi$ state are equal to the nuclear separation of the nuclei in normal $X^1\Sigma$ state. Further J. Okubo and H. Hamada take it for granted that the dissociation energy of the nitrogen molecule in the $X^1\Sigma$ state is greater than the excitation energy for the $A^3\Sigma$ v 8 state. The exact determination of these energies is very necessary, since their values are nearly equal to each other. Their whole hypothesis falls to the ground, if it be shown that the energy or the $A^3\Sigma$ v 8 is greater than the energy of dissociation.

G. Cario[20] who with Kaplan[18] had assumed the existence of metastable molecules and metastable atoms to explain the emission bands ef active nitrogen now considers that active nitrogen is atomic in nature and recombination of two normal nitrogen atoms to molecules is possible only in triple collision Molecules so produced are in an excited metastable state. Collision between two such molecules gives rise to a metastable ^2P atom and normal ^4S atom, or two atoms in the ^2D state and a normal moleonle in each case. These metastable atoms collide with metastable molecules raising them to higher energy levels from which they emit the afterglow bands.

The arguments advanced for the production of metastable molecules and metastable atoms are worthy of careful attention. Cario accepts 7·34 volts as the value of the dissociation energy as determined by Sponer and Herzberg[19], and 6.14

volts as the value of the ground level of the A state as against 9 and 8·3 volts respectively. So far as the mechanism of the emission of the afterglow is concerned the quantitative data do not matter, although it may be remarked that the accuracy of these data is questioned by some experimenters[6] and supported by many others. To follow Cario then, two normal atoms and one normal molecule meet in a triple collision. In their recombination process, they liberate 7·34 volts of energy which raises the molecule to $A^3\Sigma\, v^7$, or to $A^3\Sigma\, v^0$. In the latter case the difference (7·34–6·14) will be used partly by the old and partly by the new molecule to change their translation energy. Metastable atoms are produced by collision of two metastable molecules. For a ^2P atom the reaction would be

Volts.		Volts.		Volts.		Volts.		
6·14	+	6·14	=	7·3	+	3·56	+	a small part.

The small amount of energy which remains unaccounted for would be used up by a ^2P atom to change its translation or vibrational energies. For a ^2D atom,

$$6{\cdot}14 + 6{\cdot}14 = 7{\cdot}3 + 2{\cdot}37 + 2{\cdot}37.$$

In this case a very small amount would be left for changing the translation or vibrational energies.

It will be seen from the above reactions that in the collision between metastable molecules the number of ^2D atoms produced on an average should be twice as great as the number of ^2P atoms produced. Interpreted spectroscopically this means that in the spectrum of active nitrogen, bands from $B^3\pi\ v^6$, $B^3\pi\ v^5$ etc. should be more intense than those arising from $B^3\pi\ v^{11}$ etc. This is quite in contradiction to the observed distribution of intensity in the afterglow, where, bands arising from $B^3\pi\ v^{11}$ being the most intense, ^2P atoms must obviously be the more abundant of the two. This constitutes clearly a contradiction between experience on the one hand and theory on the other. Cario's present hypothesis is still open to the objection that no impact

resonance in metallic vapours is experienced, in spite of the production of metastable atoms and molecules in the process.

It will be clear from the foregoing pages that although there is no doubt as to the atomic nature of active nitrogen, the special enhancement of the bands arising from $B^3 \pi\ \nu^{11}$ state is still inexplicable. Of the two assumptions made by J. Okubo and H. Hamada, one at least has now the experimental backing after the determination of dissociation energy at 7·34 volts by Sponer and Herzberg which is greater than the excitation energy for $A^3 \Sigma\ \nu^{8}$ state. As has been shown before, their other assumption is still very unconvincing, and as such the special enhancement of the bands arising from $B^3\ \pi\ \nu^{11}$ state cannot be explained, as they claim, on the Franck-Condon principle. We could, of course, see from Cario's theory that the bands arising from $B^3 \pi\ \nu^{11}$ and $B^3 \pi\ \nu^{6}$ should be more intense than those arising from other levels of $B^3 \pi$ state. But looking to the proportion in which the metastable atoms in the ^2P and ^2D states are produced according to Cario's theory, the bands arising from $B^3 \pi\ \nu^{6}$ should be the most intense—a conclusion falsified by experiment. Cario's theory is still open to the objection, that in spite of the production of the metastable molecules and metastable atoms in triple collisions no impact resonance in metallic vapours is experienced.

Part played by foreign matter.

It has been said in the beginning that the presence of foreign matter is very essential for the production of active nitrogen. It therefore yet remains to consider the part thus played by the small proportion of foreign gases in its production. We have seen that the afterglow bands are due to the N_2 molecule alone. The impurities play no part in the actual light emission process. Their function must therefore be in some way to accelerate the formation of atoms into excited molecules in the discharge, or to retard the spontaneous reversion of the active nitrogen which, in

their absence, may be very rapid indeed. The work of Wood and Bonhœffer in their investigation on hydrogen and the process of chemiluminiscence provides us with a suitable analogy which, when applied to active nitrogen, probably explains the point in question. Wood and Bonhœffer have shown that in a discharge tube filled with slightly impure hydrogen, the gas is completely dissociated in those parts of the tube which are far from electrodes, and can be pumped in a monoatomic form by a fast pump into a connecting tube. The walls of the tube cause a catalytic recombination of hydrogen atoms into molecules, and the impurities in the gas such as oxygen etc. act so as to hinder the catalytic recombination of atoms into molecules by the walls of the tube. The 'impurities' in nitrogen could have an exactly similar effect in preventing the destruction of atomic nitrogen in a 'useless' wall reaction.

SUMMARY.

1. A short account is given of the properties and phenomena of active nitrogen and also of the different methods of producing it. It is shown that the first prositive system, $B^3\pi \rightarrow A^3\Sigma$ is due to N_2 molecule.

2. Three possible views of the mechanism by which active nitrogen is produced and suffers decay are discussed. It is now admitted that active nitrogen is atomic in nature, but none of the two theories discussed in the article explains convincingly the special enhancement of the bands arising from $B^3\pi$ ^{11}state.

3. An account is given of probable part played by foreign matter which is essential for the production of active nitrogen.

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